46. *The Oxidation of Carbonyl Sulphide.*

By C. E. H. Bawn.

During the last few years numerous reactions have been discovered which exhibit sharply defined limits of pressure separating regions of slow reaction from those of explosive change. Such reactions are chain reactions and can be satisfactorily explained by Semenoff's chain-branching theory (*Z. Physik*, 1927, **46**, 109; 1928, **48**, 571). Our knowledge of the actual nature and characteristics of these chains, however, is still scanty, and further evidence with regard to their origin, propagation, and destruction is desirable. Much information concerning the stopping of the chains has been obtained from observations of the effect of inert gases on the explosive reaction. Generally, the diluent acts so as to cause an increase in the reaction rate, or a decrease in the lower explosion limit, by preventing the diffusion of the chains to the wall of the vessel where they are deactivated. In the present investigation, however, the influence of helium, argon, and nitrogen caused an increase in the lower explosion limit. This is most probably due to the effect of the inert gases on the surface reaction which ultimately leads to the initiation of chains in the gas. Further, the effect of varying diameter of the reaction vessel shows that the chains are broken at the surface of the vessel. The inert gas plays, therefore, the dual rôle of delaying the actual initiation of the chain and facilitating its propagation, when once started, by preventing deactivation at the wall.

Experimental.

Apparatus.—The reaction vessel consisted of a cylindrical quartz tube, connected by means of capillary tubes to a gas burette and to the pumping system. The burette was also in connexion with a large glass storage vessel containing the gas mixture. The O and COS were stored in glass gas-holders, which were also connected to the gas burette in order that the separate gases or the mixture could be admitted to the reaction vessel. The vessel was heated in a specially wound electric furnace (30 cm. long and 5 cm. in diam.), which was enclosed in a sheet-iron casing (30 cm. long and 28 cm. in diam.), the inner space being packed with kieselguhr. The temp. was measured by means of a Pt–Rh thermocouple and a millivoltmeter, which had been previously calibrated : it was const. (to within 1°) over the central part of the furnace (20 cm.) during long periods. The press. in the system was determined by a capillary Hg manometer, attached directly to the reaction vessel, a Pye travelling microscope being used as measuring instrument. The manometer was cleaned frequently on account of the deposition of S on both the glass and the Hg surface.

Three reaction vessels, *A*, *B*, and *C*, with the following dimensions were employed : *A*, vol. 148·2 c.c., diam. 3·7 cm.; *B*, vol. 76·9 c.c., diam. 2·4 cm.; *C*, vol. 35·0 c.c., diam. 1·4 cm. The vessel *D* was of the same dimensions as *A* but was packed with small glass spheres.

Preparation of Gases.—O was obtained by heating pure $KMnO_4$ and dried by passage over P_2O_5. COS was prepared as previously described (Lochte-Holtgreven and Bawn, *Trans. Faraday Soc.*, 1932, **28**, 698), and was further purified from H_2S by passage through acidified $CuSO_4$ aq. It was dried by P_2O_5 and stored over HgO. N, A, and He were obtained directly from cylinders and dried as before. The gases were free from all combustible gases.

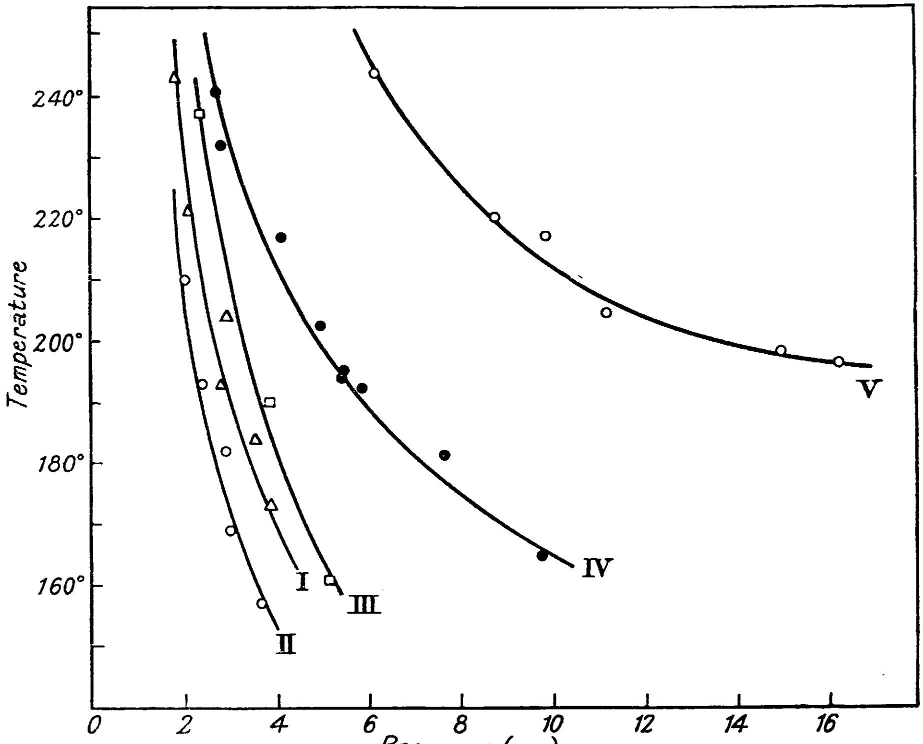
Procedure.—Since a decrease in vol. occurs on reaction, the change was followed directly. Known vols. of gas were admitted from the gas burette to the evacuated vessel, and the press. read. This was done as quickly as possible, and any single admission was completed within 5 sec. Since the vol. of the system was known (the vol. of the connecting tubes external to the furnace was about 7 c.c.), any instantaneous combustion could be measured. However, as the explosion was accompanied by an induction period, the reaction could usually be observed directly by the movement of the Hg surface and also by the bright flame in the connecting tubes. The time of evacuation was kept const. for each expt., and the explosion limit was approached from both sides. The gases were removed from the reaction vessel by means of a Toepler pump, and analysed in a Bone–Wheeler apparatus, O being absorbed by alk. pyrogallol and CO by ammoniacal Cu_2Cl_2 aq.

Activity of Vessel, and Induction Period.—The explosive reaction was always preceded by an induction period, which varied from seconds to minutes depending on the activity of the surface of the reaction vessel. A long induction period was often observed with an inactive surface, but with an active surface it was usually of the order of 5—10 sec. No press. change was observed during the induction period, and the explosion occurred abruptly.

The variation of the activity of the surface may be attributed to two causes. (1) The explosion was accompanied by liberation of free S and possibly CS; these were deposited on the wall and caused a marked decrease in the activity of the surface and thus an increase in the lower explosion limit; after several series of explosions, the surface was rendered totally inactive and no explosions were obtained. (2) The activity was a property of the surface and depended on its previous treatment. An inactive surface could be reactivated (usually to its original activity) by heating in air for a prolonged period at 300°. In some cases the vessel was cleaned with HNO_3, and this treatment gave a more active surface.

The method of admitting the gases, although producing little change in the lower limit, had a marked effect on the induction period. With gas mixtures ($2O_2$: 1COS) the induction period was about 5—10 sec.; but when the O was admitted to the reaction vessel initially, induction periods up to many mins. were obtained before explosion, the results under these conditions, however, being not nearly so reproducible as when the mixture was used. This may be explained on the assumption that the induction period is determined by a surface reaction (p. 149), which ultimately initiates the explosion.

FIG. 1.



I. $2O_2$: 1COS. *Vessel* A. II. $3O_2$: 1COS. *Vessel* A. III. $1O_2$: 1COS. *Vessel* A.
IV. $2O_2$: 1COS. *Vessel* B. V. $2O_2$: 1COS. *Vessel* C.

The Lower Explosion Limit of COS : O_2 *Mixtures*.*—The influence of varying the composition of the mixture was investigated in vessel *A*. The ignition temp. was lowered by addition of O and raised by addition of COS to a $2O_2$: COS mixture. The results are shown graphically in Fig. 1. On account of the variability of the surface over long periods, it was necessary to check the surface activity frequently, and in all the expts. concerning the influence of inert gases on

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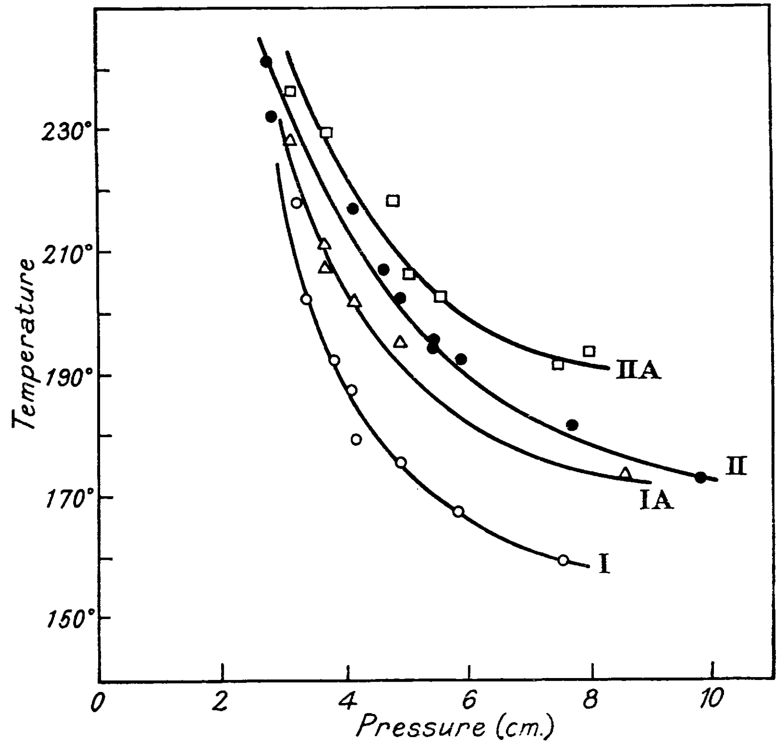
* The reaction also shows an upper critical explosion limit, but a detailed study of this was not made on account of the unsuitability of the apparatus and also because the heavy deposit of sulphur at high pressures reduced the reproducibility of the results.

the explosion limit the activity was checked either before or after each series against the standard $2O_2$: 1COS mixture.

Determination of the products of combustion showed that the reaction did not proceed according to any simple stoicheiometric relationship : as calc. from the equation $3O_2 + 2COS = 2CO_2 + 2SO_2$ it corresponded to about 80% burning of the COS. The products included CO_2, CO, SO_2, SO_3, S, and possibly CS : they were not completely analysed, only CO, residual O, and constituents absorbed by KOH being determined. With a $2O_2$: 1COS mixture, a series of analyses showed that 58—66% of the O was used, and that the unburnt CO did not exceed 5% of the total products.

Effect of Moisture on the Lower Explosion Limit.—Hadman, Thompson, and Hinshelwood (*Proc. Roy. Soc.*, 1932, *A*, **137**, 87; **138**, 292; where references to earlier work are given) have shown that the kinetics of the " dry " CO oxidation are fundamentally different from those of the " wet " reaction, and that the oxidation can take place independently of the presence of traces of moisture. They also confirmed the work of Garner and co-workers (*Trans. Faraday Soc.*, 1928, **24**, 470; 1930, **26**, 190), who showed that the explosion limit is only slightly affected by the presence of H_2O vapour. The effect of moisture on the oxidation of COS is similar in many respects to that in the case of CO. The lower limit for explosion is not appreciably altered, although H_2O vapour produces a marked influence on the induction period. Whereas with the " dry " mixture this was under 10 sec., and was greatly altered by initial introduction of O (see p. 146), yet with the " wet " gases it was usually from 60 to 80 sec. and in some series was so const. that it was possible to predict at what time explosion would occur. Furthermore, in contrast to the " dry " explosion, in which no reaction could be observed during the induction period, in the wet mixture a slight press. decrease was observed, although explosion still set in abruptly. This indicates that a reaction is occurring during the induction period and probably on the surface, *e.g.*, $COS + H_2O \longrightarrow CO_2 + H_2S$. In these expts. the procedure was to admit the O, saturated with H_2O vapour (this was included in the O pressure), to the reaction vessel

FIG. 2.



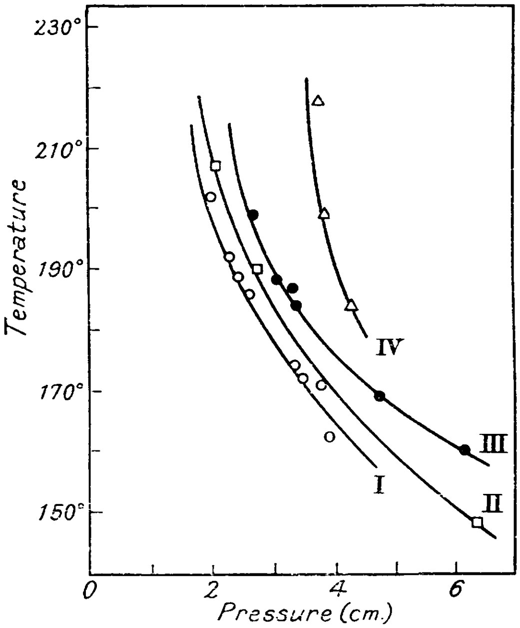
I. $2O_2$: 1COS. *Vessel* A.
II. $2O_2$: 1COS. *Vessel* B.
IA. $2O_2$: 1COS + 15% A. *Vessel* A.
IIA. $2O_2$: 1COS + 25% A. *Vessel* B.

before the COS. Some results for a $2CO_2 : 1COS$ mixture containing 13 mm. of H_2O vapour, together with the results of a dry $2O_2 : 1COS$ mixture carried out under the same conditions (O admitted before COS), are tabulated below.

" Wet " gases.		" Dry " gases.			
Temp.	Lower explosion press., cm.	Temp.	Lower explosion press., cm.	Temp.	Lower explosion press., cm.
182°	4·30	181°	4·57	163°	10·00
228	2·43	218	2·34	172	4·74
194	4·00	171	4·64		
209	2·93				

Influence of Vessel Dimensions.—The effect of changing the diameter of the vessel was studied in vessels *A*, *B*, and *C*. The ignition limit was markedly increased by a decrease in the diam. of the vessel, and was completely inhibited in a vessel packed with small glass spheres. The results are shown in Fig. 1 : they indicate that the reaction chains are broken at the surface of the vessel.

FIG. 3.



I. $2O_2 : 1COS$.
II. $2O_2 : 1COS + 15\% \ N_2$.
III. $2O_2 : 1COS + 15\% \ He$.
IV. $2O_2 : 1COS + 25\% \ He$.

Influence of Inert Gases.—The effect on the lower limit of various proportions of He, A, and N was investigated with a $2O_2 : 1COS$ mixture. The results are given in Figs. 2 and 3, together with the standard $2O_2 : 1COS$ curves. The presence of the inert gas invariably raised the explosion limit. As far as can be deduced from the exptl. data, the effect is greater the wider the vessel and the higher the press. of inert gas. The effectiveness decreases in the order He>N>A.

Surface Reaction.—It has been stated that no measurable stationary reaction occurs below the lower explosion limit and up to 230°. In view of the fact that the initiation of the explosion is dependent on the condition of the surface of the vessel, it is highly probable that a surface reaction is occurring during the induction period, and that this ultimately sets up the reaction chains. This reaction may be slow under the conditions of the expt., but should be increased by increase of surface. This was confirmed by packing the vessel *A* with small glass spheres. A measurable but slow reaction occurred at 250°. For instance, with a $2O_2 : 1COS$ mixture at an initial press. of 10·38 cm., a decrease of 0·41 cm. occurred in 37 min. With O or COS alone, no measurable alteration of pressure was observed. The kinetics of this reaction was not studied, since at temps. at which it becomes appreciable the COS itself begins to decompose and many complicating side reactions occur (Stock, *Ber.*, 1924, **57**, 719).

Photochemical Reaction.—Lochte-Holtgreven and Bawn (*loc. cit.*) have shown that the molecule of COS is decomposed by light of $\lambda = 2550$ Å. into a normal CO molecule and an excited S atom. If the thermal reaction chain involves either of these products, it should be possible to accelerate it by photochemical means and possibly displace the limit. Expts. were therefore carried out with gas mixtures at pressures just below the explosion limit and at temps. from 18° to 160°. The source of light was an air-cooled Hg-vapour lamp, using 2·5 amp. and 220 volts. The light was focused to the centre of the quartz reaction vessel by means of suitable quartz lenses. In no case did a press. change of more than 1 mm. occur, even with gas mixtures at 160° and periods of illumination up to 12 hr. These results were verified by the use of a specially constructed tube fitted with optically worked quartz windows. Even with a water-cooled H discharge tube as a source of illumination, no appreciable reaction occurred at room temp., and analysis of the gases showed that no O was consumed and the decomp. of the COS, as determined by the amount of CO formed, did not exceed 5%. The slight amount of decomp. can be attributed to the deposition of a film of S on the window which completely stopped all the ultra-violet light active in the decomp. This was also found to be the case with CS_2,* which, as Thompson has shown (*Z. physikal. Chem.*, 1931, *B*, **14**, 359), is also photochemically inactive towards O below the explosion limit. With a tube 10 cm. long containing CS_2 vapour at 4 cm. press., ultra-violet light transmitted through the tube, as examined by a fluorescent plate, was stopped completely after 10 mins.' illumination.

A deposit of S was visible on the window, as with COS. In spite of the slight amount of decompn. it seems reasonable to assume that neither of the reactions, $COS \longrightarrow CO + S'$, $CS_2 \longrightarrow CS + S'$, can lead to chain formation in CS_2– and COS–O mixtures; *i.e.*, the S atom in the ^1D metastable state does not react with O_2 molecules to any appreciable extent. The reaction probably requires a considerable activation energy, as has been found for the reaction of O atoms towards H_2 and CH_4 molecules by Kistiakowsky and others (*Chem. Rev.*, 1932, **10**, 90).

The Carbonyl Sulphide Flame.—It has long been known that the initiation and propagation of flame in a CO–O mixture is largely dependent on the moisture content of the gases (Bone and Townend, " Flame and Combustion in Gases "). Recently, Bawn and Garner (J., 1932, 129) have shown that in quartz explosion vessels unstable flames are produced with H-free mixtures, and that above a certain critical press. H-containing gases give rise to stable flames. A similar exptl. method has now been used to study the influence of gases on the lower explosion limit for the oxidation of COS. An ordinarily dried $2O_2$: 1COS mixture shows a definite limit at approx. 4·6 cm., but this was found to be dependent on the moisture content of the gases. It has not yet been possible to control these conditions on account of the great difficulty of removing the last traces of H_2S from the COS. However, by carefully drying the gases over long periods it has been possible to produce unstable flames, and in some cases to prevent flame entirely. In one expt., in which a mild spark was used for ignition, no flame was obtained after continued sparking, but after the tube had been slightly warmed (in order to liberate a trace of moisture) and then cooled, sparking caused a slow flame to be propagated along the whole length of the tube. In all cases the effect of drying was to decrease the speed of flame. Further expts. are now being carried out on the catalytic effect of H and other gases on the explosion at the lower limit.

DISCUSSION.

Induction Period.—The induction period or " time lag " which precedes explosion in heated vessels has been observed previously in many cases (see Bone and Townend, *op. cit.*, Chap. VIII); the evidence indicates that it is primarily due to a period of " preflame " combustion which occurs on the surface of the vessel. The importance of this surface combustion on the ignition phenomena was first emphasised by Garner (*Trans. Faraday Soc.*, 1928, **24**, 470; 1931, **27**, 176), who showed that the explosion is determined by the velocity of two different types of reaction : (1) a heterogeneous and a homogeneous reaction in the gas layers adjoining the wall, and (2) a thermal reaction in the gas. He concluded that the extent of the lowering of the ignition temperature by the silica surface is determined by the temperature of the surface layers, and that a high rate of surface reaction corresponds to a low ignition temperature. The surface origin of the chains has since been clearly demonstrated by the work of Alyea, Lewis and Feitknecht, and others (see Lewis, *Chem. Rev.*, 1932, **10**, 51), and this appears to be a universal phenomenon in thermal explosions. According to Garner's theory, the initiation of the chains into the gas occurs when the rate of surface reaction exceeds a certain critical value. This leads to a very simple interpretation of the induction period : it is the time necessary for the rate of surface reaction to attain a value such that the emission of reaction carriers into the gas sets up chain branching. The rate of this reaction will be dependent on the activity of the surface and also on the relative adsorbabilities of the reactants. This explains the phenomena observed.

Influence of Inert Gases.—The effect of varying the diameter of the reaction vessel shows that the chains are broken at the surface of the vessel. It would be expected, therefore, that the influence of inert gases would be to cause a decrease in the explosion limit. On

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* This observation was made by Dr. W. Lochte-Holtgreven, to whom the author expresses his thanks for assistance with the photochemical work.

the contrary, nitrogen, argon, and helium cause a marked increase in the lower critical limit. Since the inert gas is not appreciably adsorbed on the silica surface at the temperature of the experiments, it is unlikely to have any effect on the heterogeneous part of the reaction. The action must be exerted in the gas layers adjoining the wall or in the body of the gas. It is necessary to consider these two effects independently.

(1) It has been stated previously that the initiation of flame is governed by the rate of surface reaction. The influence of inert gases on this reaction will be, as Garner (*Trans. Faraday Soc.*, 1931, **27**, 176) has shown, (*a*) to reduce the temperature of the surface layer by virtue of its specific heat, and (*b*) to compress the chains to within a shorter distance of the wall. Effect (*a*) is very important during the induction period, since the inert gas by virtue of its high thermal conductivity will bring about a lowering of the temperature of the film, and hence higher gas pressures are necessary for the initiation of flame. The effect of the inert gas would therefore be greater the higher its thermal conductivity, and this agrees with the determined experimental order. Similar results have been obtained by Lewis and Feitknecht (*J. Amer. Chem. Soc.*, 1931, **53**, 2911, 3565) for the influence of inert gases on the explosion of ozone catalysed by bromine and hydrogen bromide, but in these reactions the transition from slow to explosive reaction is not abrupt.

(2) The second effect, which results in a higher temperature in the surface layer, is not of great importance in the present instance, since calculation * shows that the chains are very long and spread throughout the gas. The increased number of chains confined to the wall area will therefore be comparatively small.

Since the reaction chains are broken at the surface, the presence of the inert gas, which decreases the mean free path of the molecules in the mixture, will prevent diffusion of the chains to the walls. If this effect alone occurred, a decrease in the lower explosion limit would be expected, as observed by Dalton and Hinshelwood (*Proc. Roy. Soc.*, 1929, *A*, **125**, 263) and Melville and Ludlam (*ibid.*, 1931, *A*, **132**, 108) on the lower oxidation limits of phosphine and phosphorus vapours respectively. Also, the inert gas may bring about a deactivation of the reaction " carrier " or one of the steps in the chain. Both these effects may occur, and consequently the interpretation of the results is difficult. The conclusion reached from the experimental evidence is that the principal action of the inert gas is exerted on the surface reaction or on the layers adjacent to the wall, and not on the chains, although the above effects come into play once the chain is started.

Reaction Mechanism.—Although it is not yet possible to give a complete account of the elementary reactions constituting the chain, the following simple interpretation explains the phenomena occurring. Carbonyl sulphide and oxygen combine on the wall of the vessel to form an unstable compound, which either diffuses into the gas or decomposes spontaneously and ejects energy-rich molecules (or atoms) into the gas, initiating a reaction chain. The propagation of the chain is facilitated by oxygen and inhibited by excess of carbonyl sulphide : this effect is consistent with an unstable peroxide constitution, COS,O_2, for the intermediate compound. After leaving the wall, this active molecule collides with either an oxygen or a carbonyl sulphide molecule, giving rise to different products, *e.g.*,

$$CO_2 + SO_2 + O \xleftarrow{O_2} COS,O_2 \xrightarrow{COS} COS + CO + SO_2$$

In the first case chain branching may be assumed to occur: $COS + O \longrightarrow CO + SO$ (1); $SO + O_2 \longrightarrow SO_2 + O$ (2); $COS + O \longrightarrow CO_2 + S$ (3); $SO + O_2 \longrightarrow SO_3$ (4); $O + O \longrightarrow O_2$ (5).

The effect of the inert gas may be to deactivate the unstable peroxide. Assuming that a critical concentration of peroxide is necessary for chain branching to occur, we see that excess carbonyl sulphide will raise, and excess oxygen lower, the ignition limit. A similar mechanism explains the oxidation of carbonyl sulphide. In each case the

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* This calculation was very approximate and was determined from the amount of surface reaction on the assumptions (i) that each molecule reacting initiates a chain, and (ii) that the rate of surface reaction is the same for quartz and glass surfaces; since the chains were of the order of 10^6 molecules in length, a 10-fold variation of the rate of surface reaction would not invalidate the above conclusion.

carrier of the chain is probably atomic oxygen, and this assumption is supported by the work of Harteck and Kopsch (*Z. physikal. Chem.*, 1931, *B*, **12**, 327), who showed that oxygen atoms induce inflammation in carbon disulphide vapour.

SUMMARY.

(1) The effects of the diameter of the vessel and of inert gases on the lower limit for the oxidation of carbonyl sulphide have been investigated. Preliminary experiments on the influence of hydrogen on the carbonyl sulphide flame and photochemical experiments are also described.

(2) It is concluded that (*a*) the reaction chains are initiated from the surface and also broken at the surface; (*b*) the explosion limit is raised in the presence of inert gases owing to the effect of the diluent on the temperature of the surface layers.

(3) A reaction mechanism is proposed in which the reaction chains are initiated by means of an unstable peroxide formed at the surface of the vessel. The chains are broken by excess carbonyl sulphide and facilitated by excess oxygen.

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