

387. *The Catalytic Oxidation of Carbon Disulphide and Carbonyl Sulphide.*

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When mixtures of air and low concentrations of carbon disulphide were passed through a glass tube at temperatures above 140°, non-explosive oxidation occurred with simultaneous production of ozone. This homogeneous oxidation was difficult to suppress, and a study of heterogeneous oxidation, in contact with nickel sulphide, was only made possible by the addition of small amounts of ethylene to the reactants. The heterogeneous reaction was of zero order with respect to carbon disulphide.

Carbon oxysulphide (carbonyl sulphide) does not undergo homogeneous oxidation so readily, and no difficulty was found in experimenting with the heterogeneous reaction alone. This was of first order with respect to carbon oxysulphide, but was retarded by sulphur dioxide.

These observations are discussed with respect to previous data on the adsorption of gases by nickel subsulphide.

ALTHOUGH information is available concerning the explosion of mixtures of oxygen with carbon disulphide and carbon oxysulphide (Thompson, *Z. physikal. Chem.*, 1930, **10**, B, 273; 1931, **12**, B, 327; **14**, B, 359), the oxidation of these substances by contact catalysis has not been described. The fact that they can be converted into oxides of sulphur with nickel sulphide as the catalyst has been shown by one of us (Griffith, *Inst. Gas Eng.*, 1937, Publication 175, 48), and the present investigation was undertaken to study the kinetics of the reactions.

EXPERIMENTAL.

The preparation of nickel subsulphide has already been described (Griffith and Hill, this vol., p. 717). The apparatus used was similar to that employed for the hydrogenation of carbon disulphide (Crawley and Griffith, *ibid.*, p. 720), temperatures being measured with a thermocouple embedded in the catalyst. The purification of the carbon oxysulphide was carried out as before.

Oxidation of Carbon Disulphide.—A stream of air dried by phosphoric oxide was passed through a carburettor containing liquid carbon disulphide cooled with crushed ice. This part of the apparatus is shown in Fig. 1, and was designed by Dr. E. Spivey in this laboratory. Carbon disulphide vapour is drawn into the gas stream at *B* from a woollen wick dipping into the liquid in the flask *A*. The concentration of carbon disulphide in the air stream depends on the level of the top of the wick, which can be varied as desired. In order to obtain steady results over long periods, the level of the ice in the outer Dewar flask must be maintained.

About 10 g. of nickel subsulphide were heated in a hard-glass tube of 2 cm. diameter by an electric resistance furnace, and a stream of 472 c.c. per minute of air was passed through the system. The reaction products were led into neutral hydrogen peroxide solution (20 vols.) and then into methyl alcohol containing 10% of potassium hydroxide. The former solution was titrated with *N*/50-sodium hydroxide for determination of sulphur dioxide as sulphuric acid, and the latter was acidified with acetic acid and titrated with *N*/50-iodine solution to give the amount of unchanged carbon disulphide.

It was observed, however, that oxidation of carbon disulphide took place in the empty tube at temperatures above 150°, as would be expected from Thompson's results. The experimental data were not closely reproducible when obtained by rising or falling temperatures severally, but the general character of the homogeneous oxidation and the influence of changes in the concentration of carbon disulphide is shown by the curves of Fig. 2.

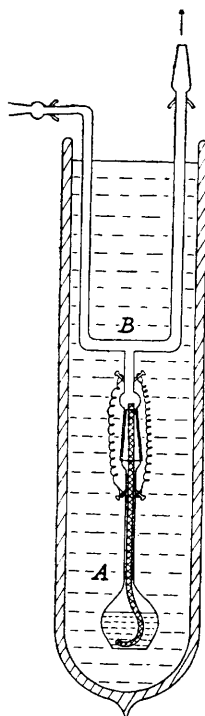
Production of ozone during homogeneous reaction. At 150–160° and 65 mg. of carbon disulphide per hour, the smell of ozone was easily detected in the reaction products. Its presence was confirmed by a positive result with the tetramethyldiaminodiphenylmethane test, and negative results with Griess reagent or with titanous chloride. Quantitative determinations with neutral potassium iodide solution gave concentrations of the order of 0.5 mg. of ozone per hour. No previous record of the formation of ozone during the slow oxidation of carbon disulphide can be found, but it is evidently due to the presence of atomic oxygen.

Separation of the homogeneous and the heterogeneous reaction. In air-carbon disulphide

mixtures, the presence of 10 g. of nickel subsulphide in the tube was without appreciable effect on the oxidation, and when the whole length of the tube (60 cm.) was packed with china-clay pellets or with glass wool, the homogeneous reaction still took place vigorously, although a temperature some 50° higher was then necessary to give equivalent conversions.

In view of the presence of ozone in the products it was thought likely that the homogeneous reaction might be inhibited by working with a lower oxygen concentration and by adding a small quantity of ethylene to the mixture. This possibility was suggested by the known effect of ethylene on the ignition of carbon disulphide; Dixon (*Rec. Trav. chim.*, 1925, 46, 305) showed that the ignition temperature of carbon disulphide in air was raised nearly 350° by the addition of a volume of ethylene equal to that of the carbon disulphide.

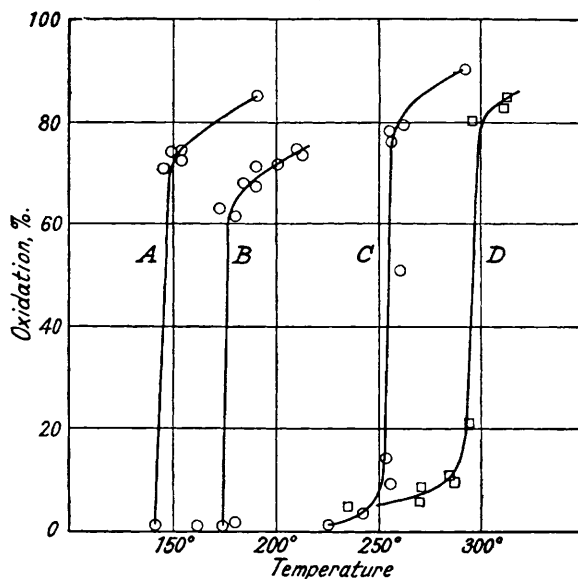
FIG. 1.



Apparatus for addition of CS_2 or COS to gas stream. Direction of gas flow shown by arrow.

Scale: two-fifths.

FIG. 2.



Oxidation of CS_2 in air.

A.	CS_2 concentration, 154 mg. per hour = 130 mg. of S.
B.	" " 65 " = 55 "
C.	" " 26 " = 22 "
D.	" " 13 " = 11 "

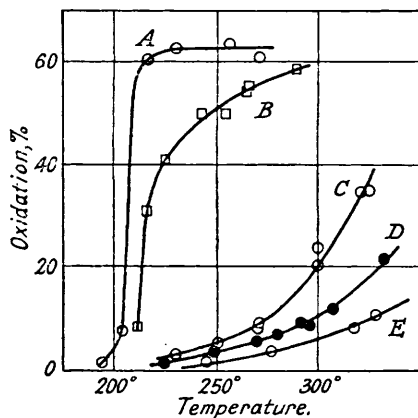
The results of a series of experiments with 1% oxygen–99% nitrogen mixtures, sometimes containing 0.14% of ethylene, and carrying varying amounts of carbon disulphide as before, are shown in Fig. 3. Under these conditions a large excess of oxygen was still present; the experiments in contact with nickel subsulphide and in presence of ethylene were found to be closely reproducible whether reaction temperatures were approached from above or below. When ethylene was present, no oxidation took place in the absence of nickel subsulphide. In the analysis of reaction products, ethylene was removed by washing with sulphuric acid after the hydrogen peroxide and before the alcoholic potash.

Curves C, D, and E of Fig. 3 show that the actual quantity of sulphur dioxide formed by heterogeneous reaction in contact with nickel subsulphide is independent of the concentration of carbon disulphide over the range explored. The heterogeneous oxidation of carbon disulphide is therefore of zero order with respect to that reagent.

Oxidation of Carbon Oxysulphide.—A stream of a mixture of 1% oxygen and 99% nitrogen was passed through the wick carburettor containing liquid carbon oxysulphide cooled to -78° , at 236 c.c. per minute. None of the usual reagents for the absorption of carbon oxysulphide was

satisfactory for quantitative determination in such low concentrations. It was necessary to add pure hydrogen to the mixture after removal of sulphur dioxide by means of hydrogen peroxide and then to burn the whole, absorbing the sulphur oxide produced in more hydrogen peroxide, and titrating for sulphuric acid with $N/50$ -sodium hydroxide in the usual way.

FIG. 3.

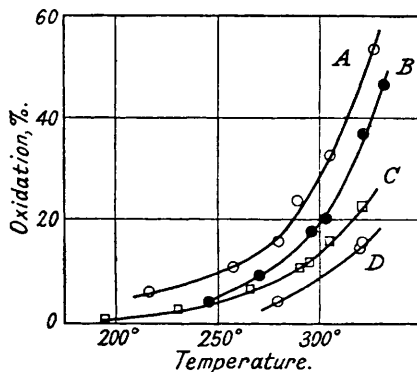


Oxidation of CS_2 in oxygen-nitrogen mixture.

A.	Empty tube ; CS_2 concn.	= 16.6 mg. per hour	= 14 mg. of S.
B.	20 C.c. of Ni_3S_2 ; CS_2 concn.	= 16.6	= 14
C.	20 C.c. " " + 0.15% of C_2H_4 ; CS_2 concn.	= 16.6	= 14
D.	" " " "	= 36.8	= 31
E.	" " " "	= 71.2	= 60

There was no indication of any gas-phase oxidation such as that found with carbon disulphide, and the results of the heterogeneous oxidation in contact with nickel subsulphide are shown in curves A, B, and C of Fig. 4. These show that the order of the reaction is apparently be-

FIG. 4.



Oxidation of carbonyl sulphide.

A.	COS concentration	= 20.6 mg. per hour	= 11 mg. of S.
B.	"	= 48.8	= 26
C.	"	= 82.5	= 44
D.	"	= 34.7	= 18.5
	+ SO_2	= 28.0	= 14

tween zero and first order with respect to carbon oxysulphide, *i.e.*, retardation of a first-order reaction occurs. Previous determinations of adsorption on nickel subsulphide (Griffith and Hill, *loc. cit.*) showed that no adsorption of carbon oxysulphide took place above 200° , but that very extensive adsorption of sulphur dioxide existed. It seemed likely, therefore, that either sulphur dioxide or carbon dioxide was responsible for the retardation.

Effect of sulphur dioxide and carbon dioxide. Experiments in which sulphur dioxide was added to the reactants (28 mg. per hour, supplied from a reservoir by way of a suitable capillary working under a constant head) are summarised by curve *D* of Fig. 4 and show that vigorous retardation is caused by this substance. An addition of 10 mg. per hour of carbon dioxide, however, was without any effect on the oxidation.

CONCLUSIONS.

The catalytic oxidation of carbon disulphide not only occurs more readily than that of carbon oxysulphide, but differences between the mechanism of the two oxidations are revealed by this investigation in conjunction with previous data on adsorption. Although oxygen is vigorously adsorbed by nickel subsulphide, the fact that the oxidation of carbon disulphide is of zero order with respect to that component suggests that the reaction occurs by collision of oxygen with adsorbed carbon disulphide. If adsorption of oxygen were also necessary, results similar to those found in the hydrogenation of carbon disulphide would have been obtained. It is unfortunately not possible to determine the order of reaction with respect to oxygen, as the catalyst would be changed to normal nickel sulphide under conditions where an excess of carbon disulphide was present.

The behaviour of carbon oxysulphide is the reverse of that postulated for carbon disulphide. Oxygen adsorbed by the catalyst reacts by collision of carbon oxysulphide, which is not adsorbed by nickel subsulphide, the amount of oxidation depending on the pressure of carbon oxysulphide but also suffering some retardation owing to covering of the catalyst by sulphur dioxide.

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