274. *The Thermal Decomposition of Carbonyl Sulphide.*

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The equilibrium conditions of the two decomposition reactions of carbonyl sulphide have been further investigated. The reaction leading to carbon dioxide is shown to be peculiarly susceptible to the nature of the vessel wall, and the rate of the reaction has been measured under various conditions. A method has been devised for measuring the rate of the fast reaction leading to carbon monoxide, and a number of velocity values have been obtained. The disproportionation of carbon monoxide, considered as a possible side reaction, is shown not to occur in the range of conditions studied.

THE thermal decomposition of carbonyl sulphide (COS) into carbon monoxide and sulphur was described by Than (*Annalen*, 1867, Suppl. Vol. V, p. 236). Lewis and Lacey (*J. Amer. Chem. Soc.*, 1915, **37**, 1976) studied the equilibrium between carbonyl sulphide, carbon monoxide, and sulphur and attributed the 16% of the gas mixture unaccounted for by their analysis to two other reactions, $2COS = CO_2 + CS_2$ and $CS_2 = CS + S$. Meyer and Schuster (*Ber.*, 1911, **44**, 1931) passed carbon monoxide saturated with sulphur through a hot tube and observed the reaction $2CO + S_2 = CO_2 + CS_2$. On heating a mixture of carbon dioxide and carbon disulphide they detected the reverse reaction and stated that the further reaction $CO + S = COS$ occurred, though carbonyl sulphide was not specifically determined. They also showed that no sulphur dioxide was formed in these reactions, though Winternitz (Diss., Berlin, 1914, quoted by Stock and Seelig, *Ber.*, 1919, **52**, 681) stated that it could be produced by the reaction $4CO_2 + S_2 = 4CO + 2SO_2$. The rôle of carbonyl sulphide in these reactions was clarified by Stock and Seelig (*loc. cit.*), and Stock, Sieke, and Pohland (*Ber.*, 1924, **57**, 719), who showed that, when carbonyl sulphide was heated alone, two independent simultaneous equilibria arose : $2COS = CO_2 + CS_2$ (" CO_2 reaction ") and $COS = CO + S$ (" CO reaction "), whilst interaction of any of the five substances in other combinations, and reactions leading to sulphur dioxide, carbon, or carbon monosulphide were negligible. Contrary to Lewis and Lacey, they found that the CO reaction was faster than the CO_2 reaction. The latter was catalysed by silica and the former proceeded to completion on a hot platinum wire. The CO equilibrium began to be measurable at 400°, while the CO_2 equilibrium was appreciable at room temperature. Klemenc (*Z. anorg. Chem.*, 1930, **191**, 246) found the CO_2 reaction entirely absent at 350°, except in one case in which the reaction vessel was filled with asbestos pellets. By calculating in terms of partial pressures some of the volumes of carbon dioxide and carbon disulphide found by Stock *et al.* (which are almost identical, as required by the CO_2 equation), Klemenc found the surprising result that the pressures of these two constituents were in the ratio 1 : 3, and so concluded that either the two equilibria could not exist simultaneously, or that they had shifted during Stock's analysis. This argument is evidently erroneous, as is seen by consideration of Klemenc's equation 2 (*loc. cit.*, p. 260).

We have further examined the variable nature of the CO_2 reaction and have shown that this is dependent on the nature and condition of the vessel wall. We have also measured the rates of both reactions under different conditions.

EXPERIMENTAL.

Carbonyl sulphide was prepared from Bender's salt (*Annalen*, 1868, **148**, 137) and dilute hydrochloric acid and was purified by passage through a bottle cooled to 0° to retain alcohol vapour, through 30% aqueous sodium hydroxide, concentrated sulphuric acid, through a trap at −55° to remove final traces of alcohol, and finally by condensation by liquid air. After evacuation, the carbonyl sulphide was distilled through a column of phosphoric oxide, head and tail fractions being rejected. The remainder was allowed to evaporate into the storage bulbs, head and tail fractions being again rejected. Six batches of about 4 l. each were prepared by this method.

Carbon dioxide from dilute sulphuric acid and sodium hydrogen carbonate was passed through two bubblers containing concentrated sulphuric acid and one trap at −70°, and condensed by liquid air. It was fractionated in the same way as the carbonyl sulphide.

Carbon monoxide from formic acid with concentrated sulphuric acid was passed through a liquid air trap and phosphoric oxide column.

Carbon disulphide from the AnalaR-quality product, shaken with mercury and redistilled, was stored in a small bulb attached to the apparatus only when required, owing to its effect on the tap-grease.

Oxygen from a cylinder was passed through a liquid-air trap and phosphoric oxide column.

The apparatus is shown in Fig. 1. The main vacuum line V was connected to a mercury diffusion pump backed by a mechanical pump. The burette B served to measure out the gases used and to analyse the products. It was surrounded by a thermostat jacket at $30° \pm 0.1°$ which also contained a levelling tube. The volume of gas could be read directly from the burette, and the pressure difference with a cathetometer.

Three reaction vessels were used, of " Pyrex," Jena glass, and silica. The first two were of the shape shown at R, and all three were provided with a similar connection at J. The " Pyrex " vessel was 27×3.1 cm., of volume 188·4 ml.; the Jena vessel was 22×3.9 cm., of volume 230·0 ml.

The silica vessel is shown inset below R in Fig. 1 (on a larger scale). It was designed to overcome the difficulty in the CO reaction due to condensation of sulphur on cold parts of the apparatus. The capillary tube from the body of the vessel was sealed by a silica plunger P with a point ground to fit the expanded end of the capillary, into which it could be tightly pressed by the tension of a piece of thick rubber tubing. The joint J connected with the rest of the apparatus, and gas could enter or leave the vessel through J and the annular space round the plunger when the latter was withdrawn a few mm. (to the right). The capillary connection and plunger valve were just outside the furnace and were kept at about 460° by a small auxiliary furnace. This valve, though not gas tight, was able to prevent diffusion of sulphur vapour into the cold parts during the short runs. Actual loss of gas was prevented by tap T_2. The volume of the vessel was 505·1 ml. and the dead space outside the valve was 2·2 ml.

Communicating with the reaction vessel was a manometer M with a levelling device whereby the mercury in the limb communicating with R could be adjusted to the same height at all pressures. In

FIG. 1.
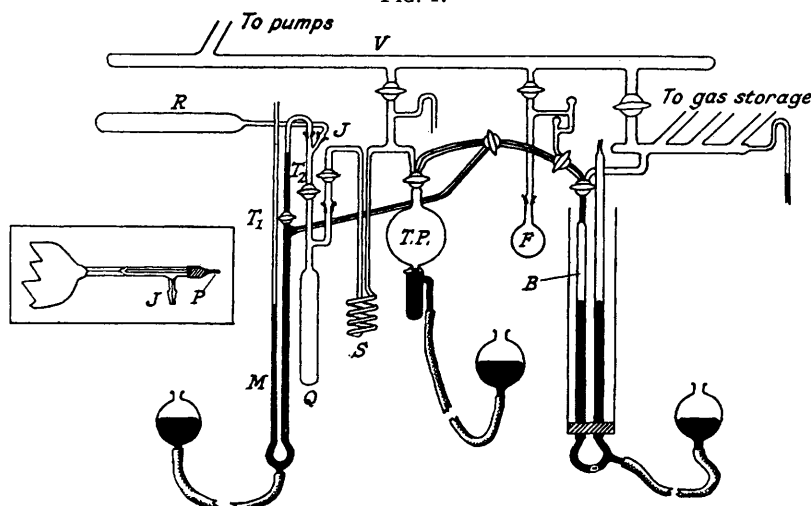
this limb was a tap T_1 and a side-arm leading *via* capillary tubing to the burette. The normal method of introducing gas into R was to measure it out in B and, after lowering the mercury in M below the side-arm, to drive the gas over completely from B, the capillary connections remaining filled with mercury at the end.

At the end of a run the gas mixture was withdrawn from R by cooling the evacuated quenching vessel Q in liquid air and quickly opening T_2. Any uncondensed gas was drawn off by the Töpler pump TP, transferred to the burette, measured, and rejected. By closing T_2 and surrounding Q with suitable cooling baths, fractions of the condensate in Q could similarly be pumped off and measured, the gas in all cases having to pass through the spiral S. Gas to be determined after absorption in a liquid reagent could be transferred from B to the flask F, subsequently detached for analysis of the resulting solution.

The reaction vessels were heated in a tubular electric furnace, 40 cm. $\times$ 8 cm. bore, being the inside of a steel tube 6 mm. thick. Temperature was measured with a platinum/platinum–rhodium thermocouple with its cold junction in ice, and a galvanometer calibrated against a potentiometer. Temperatures are given to the nearest 5°. The furnace was closed with a plug at the left-hand end, and with a slotted shield at the other. The joint J was sealed with picein wax, and at higher furnace temperatures wound over with asbestos string kept wet.

Analysis of Reaction Products.—The course of the reaction was followed by analysis since the CO_2 reaction gives no pressure change and the CO reaction is too fast to make pressure readings practicable. The resulting reaction mixture might contain carbonyl sulphide, carbon dioxide, carbon disulphide, carbon monoxide, and sulphur. On quenching in liquid air carbon monoxide alone remained and could be measured as described. Sulphur was not determined. By surrounding the condensate with a bath at $-100°$ to $-110°$, carbonyl sulphide and carbon dioxide together could be pumped off and measured, leaving the carbon disulphide in Q. The spiral S was always at the same temperature as

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TABLE I.

Run.	Vessel.	Temp.	Press., mm.	Time, hrs.	Gas used, ml. COS.	CO.	Gas found, ml. COS.	CO.	CO_2.	Reaction, %. "CO_2."	"CO."
Suppression of CO *reaction.*											
7	Pyrex	460°	748	17	72·7	—	54·5	4·0	7·55	22	7
10	,,	455	686	41	70·0	16·3	46·45	16·45	11·55	33	0
Time to reach CO_2 *equilibrium at* 450°.											
12	Pyrex	445	774	4	59·4	16·65	58·0	16·65	0·7	2·5	—
11	,,	455	805	18	62·2	16·55	53·2	16·7	4·5	23	—
13	,,	460	820	20	64·75	17·2	47·95	17·2	8·45	26	—
14	,,	440	825	39½	64·5	17·35	48·6	17·3	8·25	25	—
22	,,	450	800	68½	58·4	16·95	14·4	16·15	8·95	29	—
With silica filling.											
26	Pyrex	450	712	4	39·4	13·15	25·65	13·4	7·25	36	—
24	,,	,,	718	17	40·15	13·2	25·35	13·35	7·55	37	—
25	,,	,,	723	24	40·35	13·4	25·05	13·75	7·15	36	—
With Pyrex filling.											
27	Pyrex	450	712	4	40·2	13·15	29·05	13·1	5·55	27	—
28	,,	,,	700	18	39·6	13·05	27·5	12·85	6·1	30·5	—
35	,,	,,	735	70	41·2	13·8	29·0	13·9	6·2	30	—
With small silica filling.											
72	Pyrex	450	750	3	60·15	15·9	41·05	15·8	9·85	32·5	—
Effect of vessel wall.											
19	Jena	450	849	4	81·45	25·85	56·05	26·1	13·25	33	—
29	,,	,,	756	4	69·45	21·55	47·25	21·45	11·05	32	—
32	Pyrex	,,	771	4	42·05	14·3	31·2	14·45	5·35	28	—
33	,,	,,	754	25½	41·15	14·85	33·0	15·0	4·2	20·5	—

					Gas used, ml. CO.	CO_2.	CS_2.	Gas found, ml. COS.	CO.	CO_2.	Reaction, %. CS_2.	"CO_2."
Equilibrium approached from reverse side.												
37	Pyrex	475	725	13	22·65	37·75	32·75	45·95	22·7	15·65	9·75	37
38	,,	450	718	24	13·35	19·05	19·05	29·3	13·35	6·5	4·4	27
39	Jena	455	706	16	13·65	20·55	19·8	27·4	13·65	6·9	6·05	32

					Gas used, ml. COS.	CO.	Gas found, ml. COS.	CO.	CO_2.	Reaction, %. "CO_2."
Oxygen cleaning method.										
41	Pyrex	445	707	44	40·05	13·05	31·05	13·25	4·65	23
42	,,	445	734	41	40·6	13·0	27·55	13·2	6·55	32
43	,,	465	730	51	40·85	13·3	32·5	13·35	4·3	21
44	,,	450	711	42	40·7	13·4	28·15	13·3	6·25	31
With excess inert gas ; " Pyrex," series (a).										
53	Pyrex	450	540	7½	39·25	11·0	28·95	10·85	5·2	26
53a	,,	,,	540	,,	39·55	11·35	29·65	11·1	5·0	25
52	,,	,,	380	,,	26·5	8·3	22·55	8·05	2·0	15
54	,,	,,	315	,,	22·35	5·6	19·5	5·7	1·35	12
55	,,	,,	175	,,	12·1	4·1	11·4	4·05	0·35	6
With excess inert gas ; " Pyrex," series (b).										
51	Pyrex	450	805	7½	29·3	46·65	24·3	46·4	2·55	17
58	,,	,,	774	,,	17·9	54·5	15·65	54·6	1·1	12
71	,,	,,	705	,,	13·55	58·7	11·75	59·15	0·8	12
With excess inert gas, silica, series (a).										
70	Pyrex	450	460	2	37·25	10·55	26·0	10·45	5·65	30
67	,,	,,	280	,,	22·35	6·65	16·6	6·85	2·95	26·5
64	,,	,,	184	,,	14·15	5·15	11·2	4·95	1·45	23
68	,,	,,	113	,,	8·6	3·75	7·25	3·6	0·65	15
With excess inert gas ; silica, series (b).										
69	Pyrex	450	815	2	38·35	47·15	28·15	47·9	5·35	28
66	,,	,,	860	,,	24·85	64·75	20·45	64·8	2·15	17
65	,,	,,	880	,,	14·15	78·6	13·2	79·15	0·55	8

A few exploratory runs with CO and CO_2 reactions have been omitted.

Run.	Vessel.	Temp.	Press, mm.	Time, hrs.	Gas used, ml. COS.	CO.	Gas found, ml. COS.	CO.	CO$_2$.	Reaction, %. " CO$_2$."
Velocity coefficient, additional runs.										
74	Jena	450	452	50 min.	37·8	10·4	29·25	10·55	4·15	22
86	,,	325	330	22 hrs.	41·7	—	37·7	0·0	2·15	10·5
87	,,	,,	369	74	45·55	—	29·85	0·0	7·75	34
109	,,	400	490	4	45·8	8·5	34·6	8·5	5·65	24
108	,,	,,	495	54	44·85	10·45	28·3	10·35	8·25	37

Q, so as to retain traces of vapour which might be carried over. This was essential when pumping off carbon monoxide, which otherwise contained measurable amounts of carbonyl sulphide or carbon dioxide. The composition of the mixture of carbonyl sulphide and carbon dioxide was found by absorption in 10% aqueous potassium hydroxide, followed by conversion of sulphide into sulphate with bromine, and determination as barium sulphate. Two hours' contact of gas with solution was found to be sufficient. Various methods of determining the residue of carbon disulphide were tried without success, chiefly owing to retention of carbon disulphide by tap-grease and by sulphur formed in the reaction. Since carbon disulphide is produced in equimolecular amount with carbon dioxide, the separate determination of carbon disulphide was not necessary (cf. Stock, Sieke, and Pohland, *loc. cit.*) and the amount of carbon disulphide was assumed to equal that of the carbon dioxide.

Table I gives the results of the experiments. The gas volumes are in ml. at S.T.P., and the amount of reaction calculated as : CO$_2$ reaction = 100(CO$_2$ + CS$_2$)/(COS + CO$_2$ + CS$_2$), and CO reaction = 100CO/(COS + CO).

THE CO$_2$ REACTION.

The CO$_2$ reaction is more easily studied if the CO reaction is prevented by the prior addition of carbon monoxide. At 450° a volume of carbon monoxide equal to 25% of the carbonyl sulphide used makes the CO reaction undetectable, as runs 7 and 10 (Table I) show.

The time taken to reach equilibrium in the CO$_2$ reaction at 450° was determined by making 5 runs of increasing duration in the " Pyrex " vessel (nos. 12, 11, 13, 14, 22). These showed an approach to maximum decomposition after 70 hours, but the individual points did not lie on a well-defined curve. Stock, Sieke, and Pohland (*loc. cit.*) found equilibrium at about 40% decomposition after 4 hours ; hence our conditions were different, possibly in the nature of the surface of the vessel. Stock *et al.* found the CO$_2$ reaction to be catalysed by silica, which was confirmed by runs 26, 24, and 25, in which results in agreement with those of Stock *et al.* were found with the " Pyrex " vessel filled with silica chips (80 g.; 10—20 mesh; boiled with aqua regia), the vessel and filling being heated in a vacuum for 2 hours at 450° before use.

The discrepancy in the results with the unfilled " Pyrex " vessel was evidently due to some specific surface influence. Increasing the area of " Pyrex " produced some acceleration, but not as much as the silica (runs 27 and 28, in which 80 g. of " Pyrex " chips, prepared in the same way as the silica, were used). Even with 70 hours' contact with the increased " Pyrex " surface, the maximum decomposition was no nearer the value obtained with silica (run 35). The greater catalytic power of silica appears in run 72 in which 4 g. of silica chips produced, in a shorter time, a greater decomposition than the full " Pyrex " filling.

A few runs (*e.g.*, nos. 19, 29) showed that the Jena glass vessel was almost as effective as the silica, the decomposition being over 30% in 4 hours. Run 29 was carried out some time after run 19 ; immediately following run 19 some similar runs with the Jena vessel produced hardly any decomposition (about 1%). Freshly prepared carbonyl sulphide and carbon monoxide gave the same result. Two runs with the " Pyrex " vessel with " Pyrex" filling (nos. 32, 33) were then made under otherwise similar conditions ; the first was successful (cf. no. 27), and the second gave less decomposition in a longer time.

It was evident that contamination of the surface was inhibiting the reaction, this effect being much more marked with " Pyrex " than with silica. Approach towards equilibrium from the reverse direction gave a similar result ; run 37 (silica filling) giving an equilibrium corresponding to 37% decomposition, run 38 (" Pyrex " filling) 27%, and run 39 (Jena vessel) 32%. (In these reverse runs the carbon disulphide was calculated as the remainder of the initial carbon disulphide after deduction of the volume converted into carbonyl sulphide, instead of being put equal to the carbon dioxide.)

Boiling the vessels and fillings with aqua regia, washing with much distilled water, and baking out at 450° under vacuum restored the activity to some extent, but heating in contact with oxygen was more effective, as is shown by runs 41—44 in which the vessel with " Pyrex " filling was alternately not cleaned and cleaned by heating at 450—500° with oxygen for 4—5 hours at 1 atmosphere. The oxygen cleaning technique was used in all subsequent runs.

Evidently the CO_2 reaction is catalysed by silica. With " Pyrex " an increase of surface area accelerated the reaction, but not to the same extent, and with the minimum " Pyrex " surface the reaction was very slow. In the unpacked " Pyrex " vessel, there might, therefore, be a proportion of homogeneous reaction. This was examined by allowing the reaction to proceed in presence of an inert gas in contact with each surface in turn. Carbon monoxide as " inert " gas was added in excess of the amount required to suppress the CO reaction. The rate of reaction was determined with the unfilled " Pyrex " vessel and with the Jena vessel with silica filling (a) with various partial pressures of carbonyl sulphide and the normal amount (25%) of carbon monoxide added, and (b) with various partial pressures of carbonyl sulphide and increasing amounts of carbon monoxide to maintain the total pressure at about 1 atmosphere. For comparison the rate of reaction was taken as the per cent. CO_2 reaction in $7\frac{1}{2}$ hours (" Pyrex ") or 2 hours (silica). The two series of runs with each surface are given in Table I and are shown graphically in Fig. 2 (" Pyrex ") and Fig. 3 (silica). The open circles
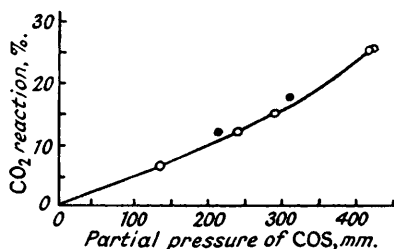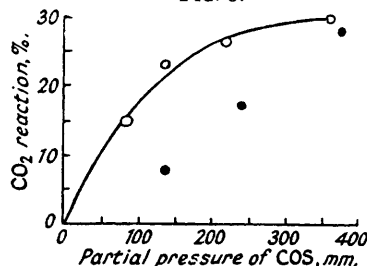
FIG. 2.   FIG. 3.

represent runs with the normal amount of carbon monoxide, and the full circles with excess of carbon monoxide.

Before consideration of these results, the velocity coefficient of the CO_2 reaction may be mentioned. The bimolecular coefficient for the reaction $2COS \rightleftharpoons CO_2 + CS_2$ was calculated for the reaction in " Pyrex " and in presence of silica from the two series (a) of the previous section, in which the normal amount of carbon monoxide was added, together with the additional runs shown at the end of Table I, with the Jena vessel with silica filling, at different temperatures and of different duration. Runs 87 and 108 give the equilibria at 325° and 400° with 34% and 37% CO_2 reaction respectively, in agreement with Stock, Sieke, and Pohland's values (*loc. cit.*). The bimolecular velocity coefficients are given in Table II.

The activation energies for the silica surface are 28,160 cals. between 325° and 400°, and 28,570 cals. between 400° and 450°, the mean being 28,450 cals.

TABLE II.

Silica surface.				" Pyrex " surface.		
Temp.	Run.	10^3k.		Temp.	Run.	10^3k.
450°	70	9·2		450°	53	1·81
	67	11·6			53a	1·65
	64	13·8			52	1·16
	68	13·0			54	0·61
	74	11·8			55	0·82
	Mean	11·9			Mean	1·20
400°	109	2·36				
325°	86	0·167				

The runs with the silica surface show that a second-order heterogeneous reaction takes place with a well-defined rate, but an interpretation of the results with " Pyrex " and Jena glass is not so easy. The CO_2 reaction rate has not previously been measured, but it is clear that its occurrence in the absence of silica is variable. It undoubtedly occurred in the work of Stock *et al.* with Jena glass, and of Lewis and Lacey with glass, but Russell (*J.*, 1900, **77**, 361) and Klemenc (*loc. cit.*) found it absent in vessels of glass and Jena glass, respectively. Gilfillan (*J Amer. Chem. Soc.*, 1922, **44**, 1329) passed carbon dioxide with carbon disulphide through a silica tube containing pumice at 400°, no carbonyl sulphide being found in the issuing gas. In the present work the reaction was found to occur and not to occur with the same surface, " Pyrex " or Jena, and the condition of the surface is responsible for this variation.

A reaction in the gas phase, if possible, would be expected to be slower than the catalysed reaction. The results with " Pyrex " indicated a much slower reaction, but since consistent results were not found with this surface, it is probable that they do not relate to a pure un-complicated homogeneous reaction. The occurrence or non-occurrence of the reaction, or its variable extent according to the condition of the surface, seems to negative a homogeneous reaction, but the experiments with excess of inert gas (Fig. 2) offer an explanation. Since addition of inert gas does not retard it, it seems that the reaction can proceed without contact with the surface. That the inert-gas technique is effective in this particular experimental arrangement is clearly demonstrated by the runs with silica (Fig. 3) which show that the reaction is, in fact, distinctly slower in presence of inert gas. At the lowest pressures with the " Pyrex " surface, however, there is an indication of acceleration of the reaction with increasing proportion of inert gas, which suggests that the surface effect enhances a subsidiary reaction re-forming carbonyl sulphide, or producing some substance emitted into the gas phase and able to inhibit homogeneous decomposition ; this effect predominates when the surface is not treated with aqua regia, oxygen, etc.

In many runs at 450° a very faint dark mirror-like deposit formed in the outlet tube of the reaction vessel, too small for detailed examination but burning off in oxygen at about the same temperature as a comparison film of carbon, and not volatilised at the softening point of " Pyrex " in the absence of oxygen. This deposit was probably carbon from traces of organic impurity, and it is possible that an even thinner deposit on the main part of the vessel was responsible for the observed surface effects.

THE REACTION $2CO \rightleftharpoons CO_2 + C$.

Stock *et al.* showed that of the possible side reactions in the decomposition of carbonyl sulphide only the decomposition of carbon monoxide was significant, and allowance was made for this. The available information on this reaction is somewhat uncertain. Deville (*Compt. rend.*, 1864, **59**, 373) stated that carbon monoxide is reversibly decomposed at a bright-red heat, and Berthelot (*Ann. Chim. Phys.*, 1879, **17**, 129) that the proportion decomposed was only a few thousandths. The equilibrium was examined by Boudouard (*ibid.*, 1901, **24**, 5) and by Fester and Brude (*Ber.*, 1923, **56**, 2245) in presence of catalysts down to lower temperatures, and Rhead and Wheeler studied the effect of temperature (*J.*, 1910, **97**, 2178) and pressure (*J.*, 1911, **99**, 1140). The reaction is exothermic and the formation of carbon dioxide is favoured at low temperatures. All these authors passed carbon monoxide over heated carbon, sometimes with addition of pumice, silica, etc., and in our experiments carbon was not initially present. Stock, Sieke, and Pohland (*loc. cit.*) with carbon monoxide alone found only slight decom-position subject to unpredictable catalytic influences, or none at all. A trace of water vapour and an increase of surface enhanced the decomposition. Cleminson and Briscoe (*J.*, 1926, 2148) found no appreciable reaction at 300° in clean glass vessels.

It was, therefore, difficult to assess the importance of this reaction and we examined it in our own apparatus under conditions similar to those used with carbonyl sulphide. A quantity of carbon monoxide was heated and the products quenched. The volume of gas (*a*) condensed in liquid air, (*b*) uncondensed in liquid air was measured. Four runs are given in Table III.

TABLE III.

Run.	Vessel.	Temp.	Press., mm.	Time.	Gas used, ml.		Gas found, ml.	
					CO.	CO_2.	CO.	CO_2.
60	Pyrex	550°	360	5 hrs.	30·15	—	30·1	0·0
62	,,	500	717	21 ,,	66·65	—	66·55	0·5
78	Silica	650	562	20 min.	123·2	—	123·05	0·3
81	,,	645	345	30 ,,	45·85	26·0	45·8	26·15

In the first three runs a negligible amount of carbon monoxide decomposed, in the fourth a mixture of carbon monoxide and dioxide remained unchanged under conditions corresponding to those of the CO decomposition of carbonyl sulphide. It was concluded that under these conditions decomposition of carbon monoxide, or reaction between carbon monoxide and dioxide, would not interfere with the main reaction.

THE CO REACTION.

Preliminary experiments showed that in short runs the CO_2 reaction was absent or negligible and could be repressed by prior addition of carbon dioxide. In the analyses, therefore, only the carbon monoxide formed from a known volume of carbonyl sulphide need be determined.

In short runs it was important to introduce the carbonyl sulphide as quickly as possible. Carbon dioxide, when added, was introduced first. As much as 90 ml. of carbonyl sulphide could be introduced in 4—5 seconds. Withdrawal of products was effected by holding open the plunger valve and the tap leading to the evacuated and cooled quenching vessel for 1 minute. Trials with carbon dioxide alone showed that all but about 1 ml. of gas was withdrawn within 5 seconds. The duration of a run was measured from 2 seconds after the beginning of admission of carbonyl sulphide to 2 seconds after beginning of withdrawal. The pressure in the reaction vessel was calculated from the volumes of gases used, the extent of decomposition and the temperature. The equilibrium was determined at 4 temperatures between 500° and 650°. Run 82 (Table IV), for example, shows 28% CO reaction at 650° after 10 minutes, and runs of twice the duration with twice the amount of added carbon dioxide gave no greater decomposition.

TABLE IV.

(All runs in the silica vessel.)

Run.	Temp.	Press., atm.	Time, min.	Gas used, ml. CO_2.	Gas used, ml. COS.	Found, ml. CO.	Reaction, %, CO.
Determination of equilibrium.							
82	650°	0·779	10	19·95	86·9	19·1	22
104	600	0·814	15	35·25	88·45	10·25	11·5
91	550	0·653	15	19·4	88·45	7·65	9
90	500	0·608	15	21·05	92·4	5·05	5·5
Velocity coefficient.							
96	600	0·592	0·75	—	89·75	7·85	9
99	,,	0·247	,,	—	37·4	1·95	5·5
101	,,	0·384	,,	—	58·85	4·2	7
89	550	0·546	5	—	89·5	5·25	5·5
93	,,	0·539	6·43	—	56·8	6·15	7
105	,,	0·810	6	—	131·45	8·6	6·5
With excess of CO_2 added.							
98	600	0·918	0·75	50·75	90·65	7·5	8
103	,,	0·795	,,	65·15	58·55	3·9	6·5
With 100 g. of silica chips.							
106	550	0·669	5	—	98·25	8·75	9
107	,,	0·505	2	—	74·8	4·95	6·5

The equilibrium constants from the first set of runs are compared in Table V with those of Stock *et al.*, which were obtained by calculation from experiments at 800° and 950° (in which the CO_2 reaction was not repressed, but allowed for by extrapolation of data obtained for this reaction up to 450°).

TABLE V.

Temp.	Decomposed, % (corr. to 1 atm.).	$10^3 K_p$.	Decomposed, % (Stock, 1 atm.).	$10^3 K_p$ (Stock).
650°	19	4·7	15	2·34
600	10	0·77	9	0·49
550	8	0·275	5	0·255
500	4·5	0·055	2·5	0·0099

The rate of the reaction was measured in the rather narrow temperature range 550—600°; above 600° it was too fast to measure and below 550° the equilibrium was unfavourable. Three runs with different concentrations made at each temperature without addition of carbon dioxide are given in the second section of Table IV. Three possible reactions may be considered : (*a*) COS $\rightleftharpoons$ CO + S, (*b*) 2COS $\rightleftharpoons$ 2CO + S_2, (*c*) COS = CO + S together with 2CO + S_2 = 2COS. Case (*b*) was evaluated by the method used by Bodenstein and Krauss (*Z. physikal. Chem.*, 1936, **175**, *A*, 295). The reverse reaction appears to be negligible, and case (*c*) is similar, so that the velocity coefficients obtained represent respectively a unimolecular forward with bimolecular reverse reaction, a bimolecular irreversible reaction, and a unimolecular irreversible reaction. Table VI shows the velocity coefficients for each case.

The mean value of *k* in each case gives an activation energy (*a*) 58,900, (*b*) 74,400, (*c*) 72,800 cals.

Addition of carbon dioxide as inert gas (runs 98, 103; Table IV) produced little diminution in velocity, these runs being otherwise comparable with nos. 96 and 101, respectively, in which no carbon dioxide was added. Two runs with silica filling (nos. 106, 107) resulted in 9% reaction after 5 minutes and 6·5% after 2 minutes. The equilibrium decomposition at the

TABLE VI.

Run.	Temp.	10^3k.			Run.	Temp.	10^3k.		
		(a).	(b).	(c).			(a).	(b).	(c).
93	550°	0·251	13·8	0·203	99	600°	1·31	196	1·26
89	,,	0·215	12·3	0·189	101	,,	1·74	161	3·62
105	,,	0·241	10·3	0·147	96	,,	2·55	138	2·10

temperature of these runs is 8% at 1 atmosphere, or 9% at the pressure of run 106, so in this run equilibrium was reached in less than 5 minutes, whilst in the unpacked vessel only 5·5% decomposition occurred in the same time (run 89). In run 107 equilibrium had not been reached in 2 minutes, so the effect of the silica filling is not very marked.

The CO reaction seems more straightforward than the CO_2 reaction, but can be studied only in a small temperature range, so that it was not possible to achieve certainty on the orders of the forward and reverse reactions by rate measurements. The reaction is not markedly heterogeneous in contact with silica, perhaps partly because in the short time there was incomplete access of the gas to the surface.