S 1. *The Combustion of Carbon: Inhibition of Secondary Reactions by Volatile Reagents added to the Oxidizing Gas.*

By J. R. Arthur and Miss J. R. Bowring.

The effects of certain volatile halogen-containing (and other) compounds on the combustion of electrode carbon at 850° is examined. All the additives increase the CO/CO_2 ratio in the combustion products, and the results are interpreted in terms of an interruption of the chain cycle responsible for carbon monoxide oxidation. The general implications of the results are discussed, particularly in relation to combustion of beds of solid fuels and the mechanism of fire extinction.

The object of this investigation was to remove some points of obscurity relating to the reactions in fuel-beds in active combustion. A fuel-bed is regarded as an assembly of particles which consist predominantly of carbon; and the state of active combustion is taken to imply that the carbon surfaces undergoing oxidation are at temperatures greater than 700°.

The mechanism of oxygen consumption in technical fuel-beds is of obvious industrial importance, but much confusion still exists as to the exact nature of the reactions involved. Bangham and Thring (*Coal Research*, Sept. 1944, 48; *Trans. Faraday Soc.*, 1946, **42**, 376), in attempting to reconcile the results of laboratory scale and technical scale investigation, advanced the hypothesis of a two-stage mechanism of oxygen consumption in fuel-beds, only one half of the oxygen being considered to react with the carbon to give (mainly) carbon monoxide, the remainder reacting with this in the gas phase to give carbon dioxide. Having regard to the major role of diffusion processes in determining reaction rates in solid–gas systems at high temperatures, it is very difficult on other grounds to explain the extremely short distance of oxygen survival in fuel-beds except by a secondary reaction of carbon monoxide with oxygen.

Since at a lower temperature range (500—600°) the wet reaction between carbon monoxide and oxygen is known to occur by a chain mechanism, attempts were later made to stop the reaction at the first stage by the use of suitable inhibitors such as chlorine and volatile compounds thereof. These experiments (Arthur, *Nature*, 1946, **157**, 732; Arthur, Bangham, and Thring, *J. Soc. Chem. Ind.*, Symposium on " Oxidation of Carbon ", 1949, **68**, 1) have shown that at temperatures between 750° and 850° the CO/CO_2 ratio in the primary products can be as high as 8 to 1. Bridger (*Nature*, 1946, **158**, 236) has reported similar results relating to somewhat higher temperatures.

An alternative approach, the study of the oxidation of electrically-heated carbon filaments in oxygen at low pressures, has led to widely divergent results. The position has been partly clarified by the experiments of Strickland-Constable (*Trans. Faraday Soc.*, 1944, **40**, 333), who has shown that thermionic emission from the carbon filament can give rise to misleading results. In agreement with the earlier experiments of Sihvonen (*Trans. Faraday Soc.*, 1938, **34**, 1062), Strickland-Constable found that carbon monoxide was the main primary product over the whole range 900—2000°. He also found the reaction to be of the first order.

The present paper examines quantitatively the magnitude of the inhibition of the $CO \longrightarrow CO_2$ reaction achieved by various chlorine (and other) compounds. The extent of the inhibition is correlated with the nature of the inhibitor and its breakdown products, the possible modes of combustion of carbon monoxide, and the probable mechanism whereby inhibition is achieved. The effects of the added compounds have been compared, under identical conditions of concentration and temperature, and under comparable times of contact. The kinetics of the primary reaction which occurs in the presence of the most potent inhibitors of secondary reactions will be dealt with in a paper to be published shortly.

Experimental.

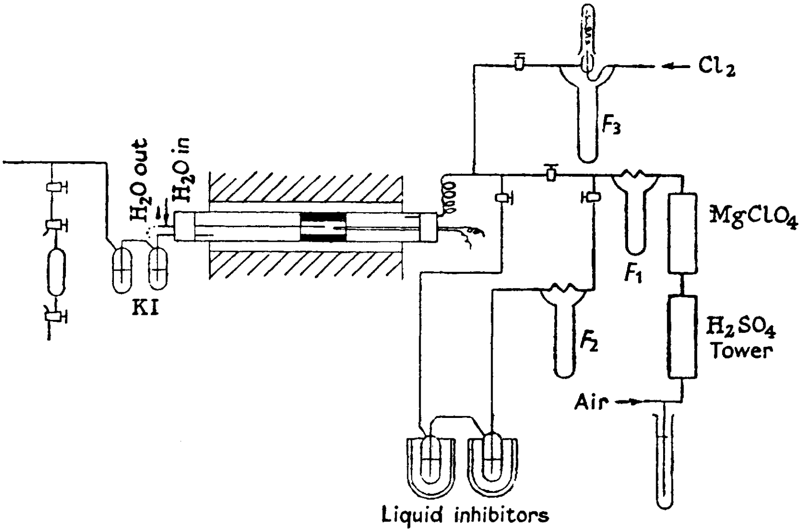
A simple flow system was used which has already been very briefly described (Arthur, Bangham, and Thring, *loc. cit.*). It is shown in Fig. 1. An electrode-carbon tube 3·0 cm. long and 1·0 cm. internal diameter was fitted tightly in a quartz tube and burnt at 850° in a tube-furnace in a slow stream of air (F_1) (300 c.c./min.) which had been dried over sulphuric acid and magnesium perchlorate. A typical analysis of the carbon tubes (supplied by the Morgan Crucible Co.) was C, 99·6; H, 0·1; Ash, 0·5; Moisture, 0·09%. Accurate determination of the hydrogen and ash contents was difficult, the former because the absolute value was very low and the latter owing to the difficulty of burning off the unreactive carbon without loss of the more volatile ash constituents (Edwards and Pearce, *Nature*, 1944, **154**, 463).

A complete analysis of the ash gave the following results:—

Constituent.	Expressed as	% of the ash.
Silica	SiO_2	29·46
Boric oxide	B_2O_3	23·40
Ferric oxide	Fe_2O_3	21·81
Ferrous oxide	FeO	1·18
Aluminium and phosphorus oxides	Al_2O_3 and P_2O_5	10·80
Calcium oxide	CaO	7·47
Magnesium oxide	MgO	2·48
Copper oxide	CuO	2·44
Manganese, nickel, cobalt, and zinc oxides	Mn_3O_4, Ni_2O_3, Co_2O_3, and ZnO	0·27
Titanium oxide	TiO_2	0·18
Alkalis	Na_2O and K_2O	2·70
Sulphur oxides	SO_3	0·39
	Total	102·58 *

* All constituents are expressed as present in their fully oxidised state.

FIG. 1.



The iron content of the ash is high, and there was presumably a release of volatile iron chlorides in the presence of inhibitors which pyrolysed to free chlorine. That the results observed were not in fact influenced by catalysis of the $CO_2 + C \longrightarrow 2CO$ reaction by these iron compounds was shown by a negligible effect of the halogen-containing inhibitors on the rate of reaction between the carbon and carbon dioxide.

The use of an unreactive tube of carbon had the advantages that (i) visible effects were easily observed as it burnt, (ii) under the flow conditions used, the geometrical surface area of the tube changed but slowly with time, allowing effectively steady conditions to be attained over sufficiently long time intervals, and (iii) there was no interference from the $CO_2 + C \longrightarrow 2CO$ reaction even at 850° (Arthur, Bangham, and Thring, *loc. cit.*).

The effects of the following inhibitors were studied : $POCl_3$, PCl_3, Cl_2, I_2, CCl_4, $SnCl_4$, CH_2Cl_2, $CHCl_3$ $SiCl_4$, SO_3, and HCl. The vapours of the liquid inhibitors were entrained by passing a portion of the main air-stream through a subsidiary flow meter F_2 and through the liquids contained in Dewar vessels at fixed temperatures. Sulphur trioxide and hydrogen chloride were entrained by passing the air-stream through oleum (containing 20% SO_3 by weight) and 36% hydrochloric acid, respectively. Chlorine gas was taken from a cylinder and measured on a flow meter F_3 with long spiral capillary choke. Iodine was entrained by passing an air-stream over a column of it maintained at 74°, the delivery tube to the furnace being kept above this temperature by electrical heating. Direct titration of the iodine showed that the air-stream was about 75% saturated with iodine by this method.

Chlorine was removed from the combustion gases by bubbling them through potassium iodide solutions. Samples of gas could be collected (i) representative of that leaving the burning tube, and (ii) which were sampled through a water-cooled tube with its gas entry at any point in the carbon tube.

The carbon tube was brought to a temperature slightly below 850° in a stream of commercial oxygen-free nitrogen. Combustion was then begun in a dry air stream. When steady conditions had been attained (as indicated by the carbon dioxide content of the exhaust gases), samples of gas were collected over 5% sulphuric acid, various amounts of the inhibitors being present in the air-stream. The gas analyses were accurate to 0·3%. Even during combustion, the temperature of the carbon tube was maintained principally by the heat input from the furnace and was kept constant to $\pm 3°$. (In later experiments the carbon tube temperature was held steady to 1—2° by a photocell-amplifier furnace control.)

Visible Effects.—When the carbon tube was burning in the air-stream, a blue luminescence could generally be observed which filled the whole cross-section of the tube, so that no estimate could be made of its thickness. It was immediately extinguished by the most minute concentration of each of the inhibitors and reappeared immediately they had been turned off. After chlorine had been passing with the air-stream, a return to combustion on air alone gave a more intense blue luminescence. This blue glow is presumably associated with some stage of the combustion of carbon monoxide, and its extinction may indicate the susceptibility of carbon monoxide combustion to inhibition.

The Effect of Concentration of the Added Materials on the Composition of the Exhaust Gases.—This is shown in Figs. 2 to 6. The curves for nitrogen were obtained by difference. No graphical data are recorded for silicon tetrachloride; although all experiments with silicon tetrachloride showed that it was an inhibitor (in some cases a potent one), reproducible results were not obtained.

The Pyrolysis Products of the Inhibitors.—Where the combustion gases contained the pyrolytic products of chlorine-containing additives, a mist of hydrogen chloride appeared over the solutions in the bubblers. Since some of the additives contained no hydrogen, this must have been obtained from the fuel or indirectly from the small quantity of moisture remaining in the air-stream.

The compounds phosphoryl chloride and phosphorus trichloride gave rise to phosphorus oxides and free chlorine. The former were deposited as finely-divided solids on the cooler parts of the apparatus. (Independent experiments in which phosphoric oxide was vaporised into a bed of carbon grains in active combustion showed that it is itself an inhibitor though less potent than the halides.) Experiments with phosphoryl chloride, using a very much shorter furnace to minimise pyrolysis, showed that it still gave a very strong inhibiting effect.

Carbon tetrachloride was pyrolysed principally to free chlorine. It was possible to account for about 80% of the total chlorine by titration of the iodine liberated from potassium iodide. Small quantities of hexachloroethane were found on the cooler parts of the quartz tube. The amounts of carbonyl chloride formed must have been small. Chloroform also gave large amounts of free chlorine in the exhaust gases. The characteristic feature of methylene dichloride and hydrogen chloride was that neither gave rise to measurable amounts of free chlorine in the exhaust gases.

The effects of sulphur trioxide are complicated by the reactions :

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$
$$CO + SO_3 \rightleftharpoons CO_2 + SO_2$$

The total oxygen content (free and combined) of the exhaust gases suggested that the sulphur trioxide was appreciably dissociated or reduced.

The Effect of Simultaneous Addition of Water or Hydrogen and an Inhibitor.—These indications of a relation between inhibiting action and a strong hydrogen or water affinity led us to examine the effects of the simultaneous addition of an inhibitor and small amounts of hydrogen-containing compounds.

Figure 7 shows the effect of increasing the water content of the air-stream containing 0·28% and 0·41% of carbon tetrachloride. The gases were sampled through a water-cooled copper tube from a point in the carbon tube, the carbon tetrachloride concentration being kept constant at 0·28% or 0·41%.

Figure 8 shows similar data for 0·32% carbon tetrachloride and hydrogen. The nitrogen curve is omitted since it cannot here be calculated by difference.

These effects are not peculiar to electrode carbon, and experiments with columns of wood charcoal, graphite, and a high-temperature metallurgical coke, under the same thermal conditions, gave similar results, phosphoryl chloride being the inhibitor used. The observations therefore appear to have a general significance. More phosphoryl chloride was required to produce the maximum effect with the charcoal than with the other fuels. This result was expected from the relative contents of volatile matter.

DISCUSSION.

Figs. 2 to 7 show that:

(1) All the added materials increase the CO/CO_2 ratio in the combustion gases.

(2) The increases in the carbon monoxide and oxygen concentrations and the decrease in the carbon dioxide concentrations are in agreement with the suppression of gas-phase reactions consuming carbon monoxide and oxygen.

(3) In all cases, these changes occur at very small concentrations ($<1\%$) of the added materials. Further additions do not appreciably alter the analyses.

(4) The added materials vary considerably in their effectiveness.

(5) The inhibition produced by carbon tetrachloride is largely destroyed by adding hydrogen or water to the air-stream: there is an abrupt, not a gradual, change in the gas composition, depending on a change of water content of about 0·2%.

The values of the ratio CO/CO_2 obtained with concentrations of inhibitors exceeding the " threshold " values afford a simple index of the inhibiting powers of the various additives. In order of effectiveness, these are:

Inhibitor	$POCl_3$	PCl_3	Cl_2	CCl_4	$CHCl_3$	$SnCl_4$	CH_2Cl_2	HCl	I_2	SO_3	None
CO/CO_2	8·4	6·4	2·9	2·6	2·3	2·1	1·1	1·16	0·59	0·52	0·05

These figures show clearly: (i) the strongest inhibitors are the phosphorus halides; (ii) Cl_2, CCl_4, $SnCl_4$, and $CHCl_3$ are roughly equal in effectiveness; (iii) the effects of HCl and

FIG. 2*a*.

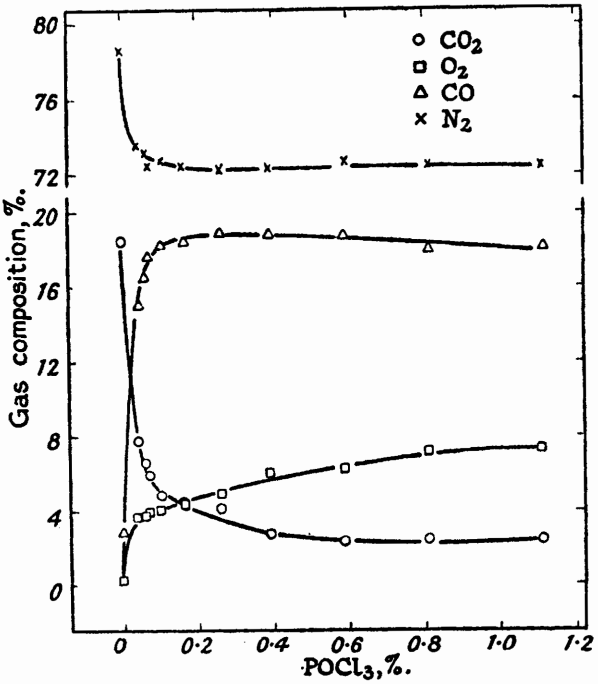

○ CO_2
□ O_2
△ CO
× N_2
Gas composition, %.
80
76
72
20
16
12
8
4
0
0
0·2
0·4
0·6
0·8
1·0
1·2
$POCl_3$,%.

FIG. 2*b*.

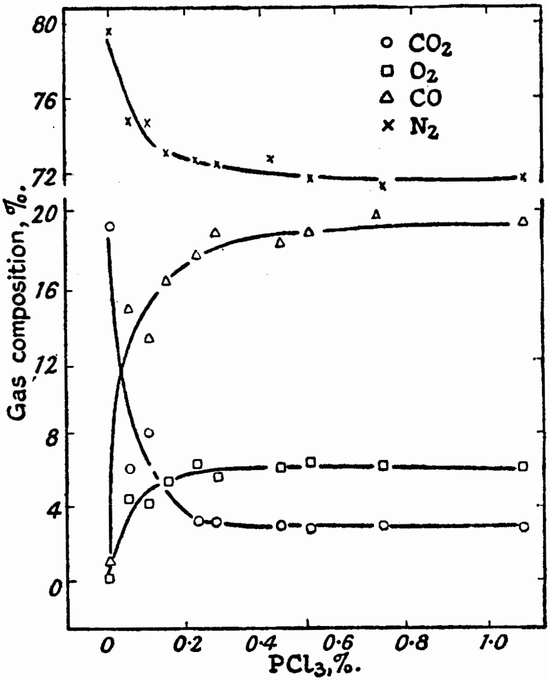

○ CO_2
□ O_2
△ CO
× N_2
Gas composition, %.
80
76
72
20
16
12
8
4
0
0
0·2
0·4
0·6
0·8
1·0
PCl_3,%.

FIG. 3*a*.

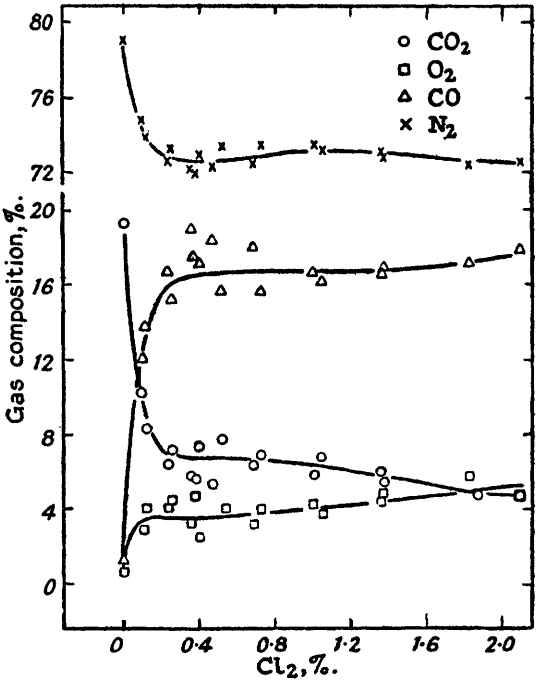

80
76
72
20
16
12
8
4
0
Gas composition, %.
○ CO_2
□ O_2
△ CO
× N_2
0
0·4
0·8
1·2
1·6
2·0
Cl_2, %.

FIG. 3*b*.

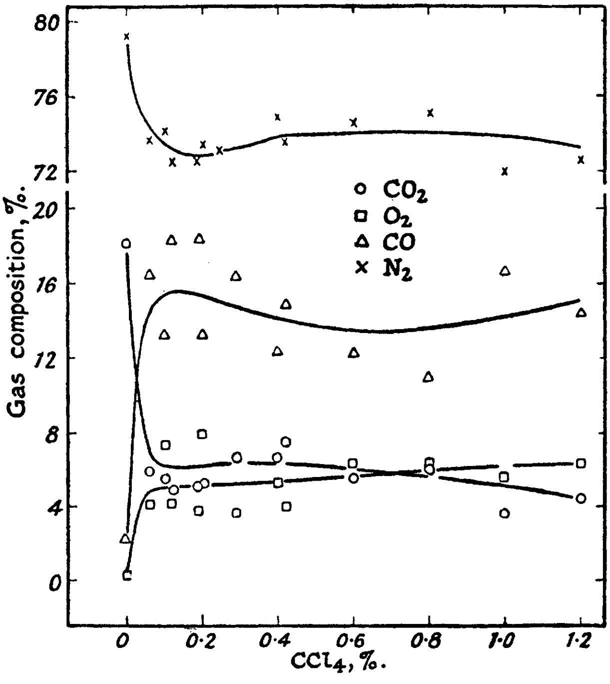

80
76
72
20
16
12
8
4
0
Gas composition, %.
○ CO_2
□ O_2
△ CO
× N_2
0
0·2
0·4
0·6
0·8
1·0
1·2
CCl_4, %.

FIG. 4*a*.

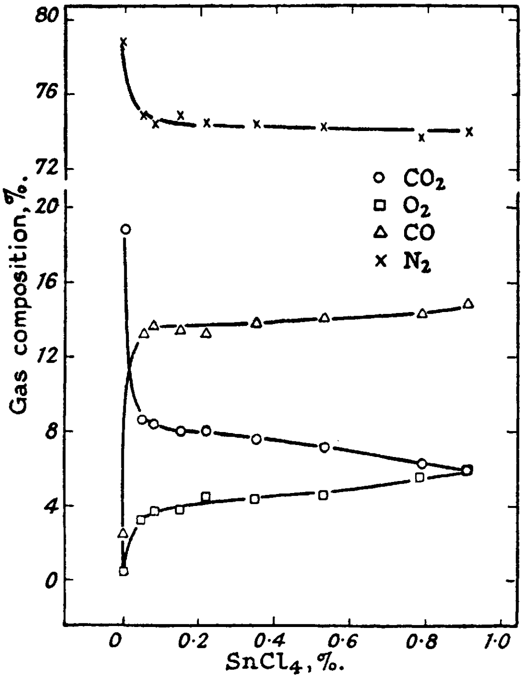

80
76
72
20
16
12
8
4
0
Gas composition, %.
0
0·2
0·4
0·6
0·8
1·0
SnCl₄, %.
○ CO₂
□ O₂
△ CO
× N₂

FIG. 4*b*.

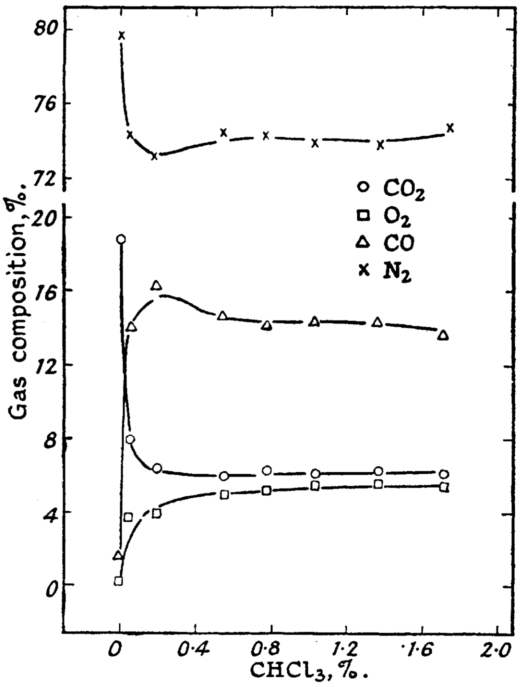

80
76
72
20
16
12
8
4
0
Gas composition, %.
0
0·4
0·8
1·2
1·6
2·0
CHCl₃, %.
○ CO₂
□ O₂
△ CO
× N₂

FIG. 5*a*.

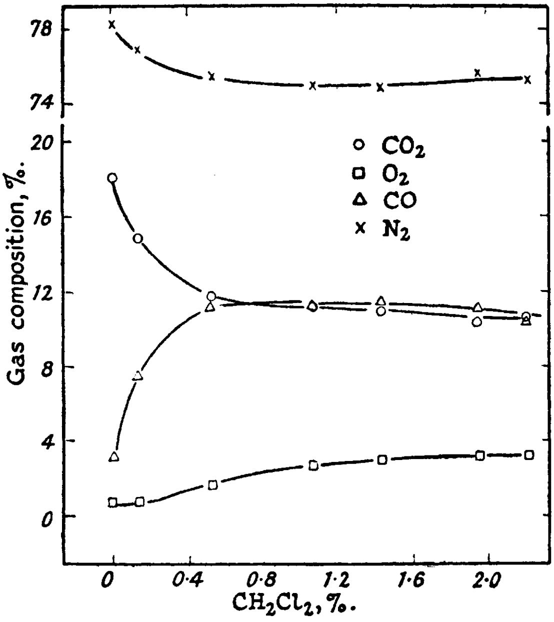
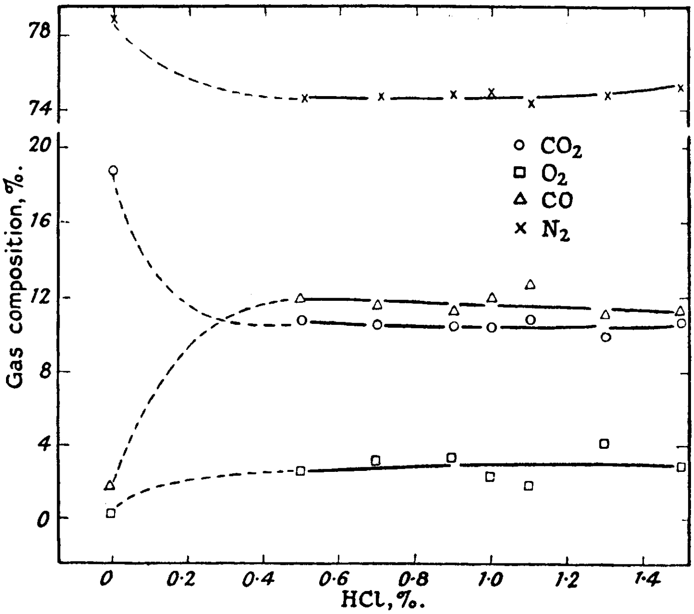

78
74
20
16
12
8
4
0
Gas composition, %.
○ CO_2
□ O_2
△ CO
× N_2
0
0·4
0·8
1·2
1·6
2·0
CH_2Cl_2, %.

FIG. 5*b*.


78
74
20
16
12
8
4
0
Gas composition, %.
○ CO_2
□ O_2
△ CO
× N_2
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
HCl, %.

CH_2Cl_2 are almost identical, although considerably less than those of the above compounds; (iv) of the two halogens used, chlorine is much more effective than iodine.

An attempt will now be made to interpret these results in the light of known facts of carbon monoxide combustion. Dixon's original experiments (*Phil. Trans.*, 1884, **175**, 617) drew attention to the significance of the role that hydrogen-containing species can have in the ignition of carbon monoxide–oxygen mixtures. Subsequent work (Bone, *J.*, 1931, 338) established the existence of dry and wet reactions, the latter accounting for the bulk of the change in all mixtures which have not been exhaustively dried. Further, the wet reaction has the characteristics of a material chain reaction in both the pre-flame and the flame region (*e.g.* the marked influence of minute quantities of added materials on flame speeds). Though the exact nature of the links in the chain still remains obscure, they almost certainly originate from the water-gas reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

FIG. 6*a*.

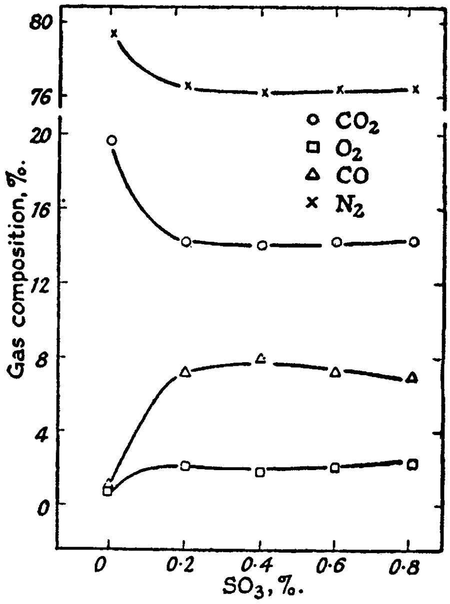
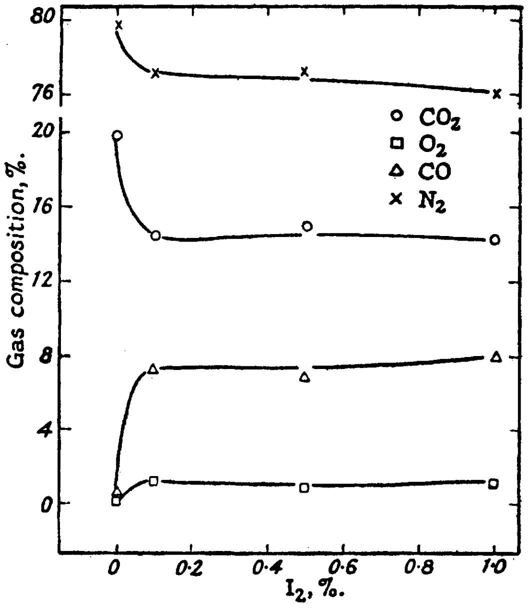


FIG. 6*b*.



if CO, O_2, and H_2O are the only molecules originally present, and thermal dissociation of the H_2O molecule is excluded. The subsequent generation of radical intermediates will be conditioned by the kinetics of the reaction of hydrogen and oxygen. Very little is known of the sequence of reactions in hydrogen flames. The OH radical is observed spectroscopically in carbon monoxide and in hydrogen flames. Evidence on the reactions in the pre-flame region is more positive. In the hydrogen–oxygen reaction, between the second and third explosion limits, the reaction

$$H_2 \longrightarrow 2H$$

has been established as responsible for chain initiation (Willbourn and Hinshelwood, *Proc. Roy. Soc.*, 1946, *A*, **185**, 353; Ashmore and Dainton, *Nature*, 1946, **158**, 416).

When carbon monoxide is also present in the system, chain propagating and branching reactions may give rise to HO_2, OH, and O.

The inhibition must be due to a reaction between the additive (or one of its degradation products) and one or more links in the reaction chain to give a stable end-product. The main source of the chain carriers is the moisture of the air-stream and the hydrogen content of the carbon. Whatever the exact nature of the links in the reaction chain, the efficiency of inhibition must be determined by: (i) the speed of the reaction between the active species and the chain link; (ii) the stability of the end-product formed from the active species and the link destroyed; (iii) the position in the reaction chain of the link removed.

FIG. 7*a*.

0·28% CCl_4 and H_2O.

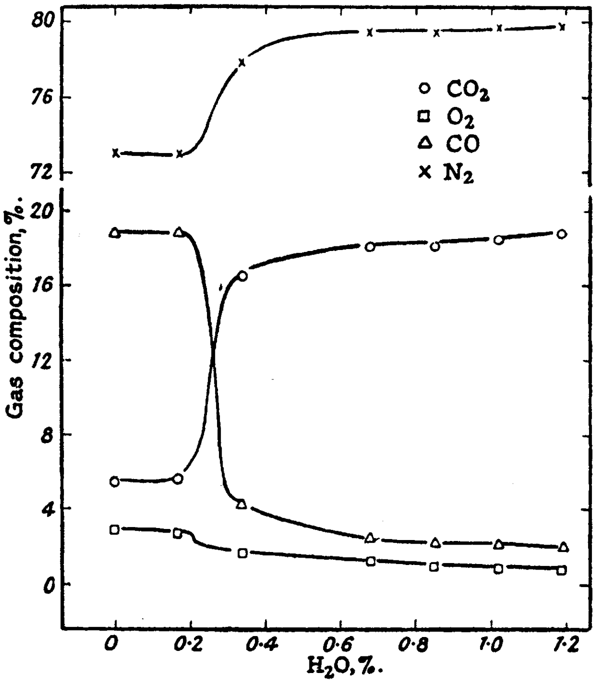
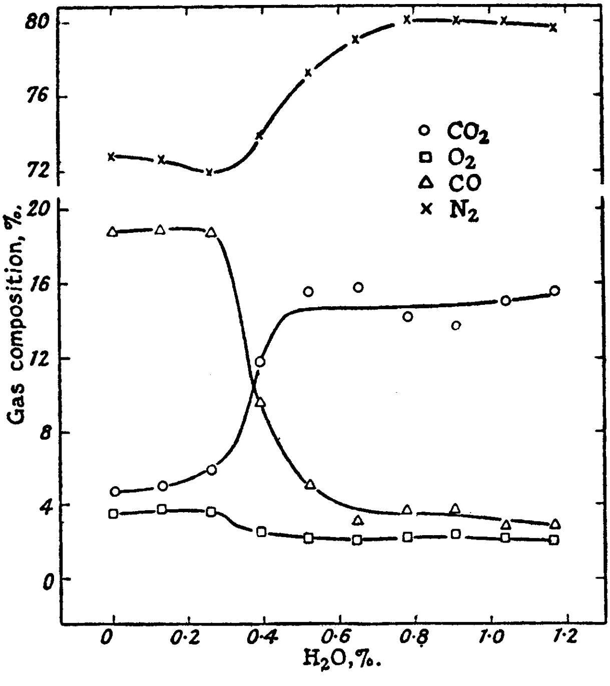


FIG. 7*b*.

0·41% CCl_4 and H_2O.



Substances with a high water affinity would be expected to increase the CO/CO_2 ratio since they are able to compete with carbon monoxide for water molecules. The phosphorus halides and sulphur trioxide are clearly examples of these:—

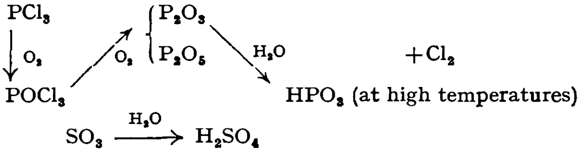
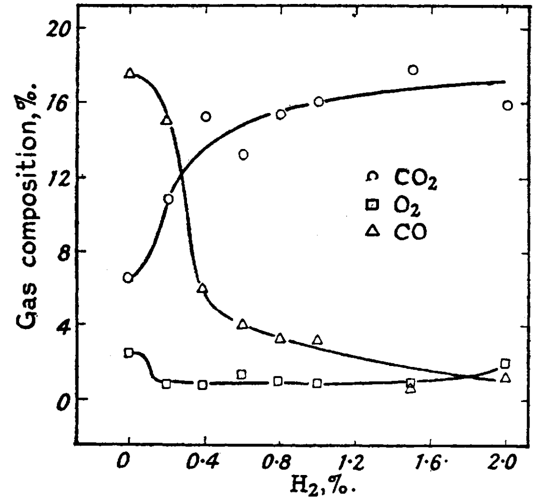


FIG. 8.

0·32% CCl_4 and H_2.



The very great difference in degree of inhibition as between sulphur trioxide and the phosphorus halides can be explained by the smaller stability at 850° of sulphuric acid compared with metaphosphoric acid, since the stability of the end-product formed between the active species and the chain link will clearly determine the capacity of the inhibitor. The overall inhibition reactions with phosphorus halides can be written:

$$2POCl_3 + H_2O + 1\tfrac{1}{2}O_2 \longrightarrow 2HPO_3 + 3Cl_2$$
$$2PCl_3 + H_2O + 2\tfrac{1}{2}O_2 \longrightarrow 2HPO_3 + 3Cl_2$$

Those substances with little or no water affinity at 850°, which give rise to free chlorine, gave a CO/CO_2 ratio of 2—2·9. They are Cl_2, CCl_4, $CHCl_3$, and $SnCl_4$. Broadly speaking they must inhibit by competing with oxygen for hydrogen. [The fall in hydrogen content of a carbon monoxide flame on addition of such inhibitors has recently been examined (Arthur and Sterling, *Nature*, 1947, **160**, 869).] The detailed reactions by which they are effective are more difficult to formulate. The inhibition reactions themselves are presumably parts of a chain cycle.

A reasonable suggestion is that the changes

$$Cl + H_2 \longrightarrow HCl + H - 0{\cdot}8\ \text{kcal.}$$
$$H + Cl_2 \longrightarrow HCl + Cl + 45{\cdot}0\ \text{kcal.}$$

compete for H_2 and H with reactions that result in the propagation and branching of the chains. In view of the lack of data, it is not possible to be more precise than this.

The much smaller effect of iodine can be interpreted in terms of the smaller stability of hydrogen iodide compared with hydrogen chloride.

The remaining two chlorine compounds (hydrogen chloride and methylene dichloride) gave identical CO/CO_2 ratios of 1·1. Pyrolysis and oxidation of methylene dichloride at 600° is known (Whittingham, unpublished data privately communicated) to give carbon and hydrogen chloride so the identity in results is to be expected. Of the possible chain links in carbon monoxide combustion, the most likely one with which hydrogen chloride can react easily is H.

If the change $HCl + H \longrightarrow H_2 + Cl + 0{\cdot}8$ kcal. conditions the initiation of inhibition by hydrogen chloride, it is understandable that the effect observed should be less than with, say, chlorine which can attack an earlier stage in the reaction chain (*viz.* molecular hydrogen).

More general implications of the above results are as follows :

(i) Evidence as to the possible role of hydrogen or moisture on the primary surface reaction between carbon and oxygen cannot be obtained when these chemical inhibitors of secondary reactions are present. There is no positive evidence however that the primary reaction between carbon and oxygen is different when these inhibitors are present or absent. Indeed, a partial inhibition of secondary reactions has been achieved (Arthur, Bangham, and Thring, *loc. cit.*) by a solid surface (silica) remote from the carbon surface.

(ii) Since the inhibitors used vary considerably in their effectiveness, some of the residual carbon dioxide found when certain of them are present is due to failure to prevent normal " wet " carbon monoxide oxidation. With phosphoryl chloride, however, this is not necessarily the case. The alternative sources of the carbon dioxide are : (*a*) the dry homogeneous reaction between carbon monoxide and oxygen; (*b*) the heterogeneous thermal reaction between carbon monoxide and oxygen; (*c*) a direct heterogeneous reaction between carbon and oxygen. Experiments are now in progress which should enable a decision to be made between these various alternatives.

(iii) A long reaction chain indicates that the chain carriers are regenerated with a high efficiency. Under these conditions, and especially if the tendency to branch is considerable, the concentrations of inhibitors required to prevent reaction will be very small. This is clearly the state of affairs shown in the figures, *e.g.* 0·04% of phosphoryl chloride vapour reduces the carbon dioxide content of the exhaust gases from 18·5 to 7·8% and the maximum retarding effect is shown by about 0·5% of phosphoryl chloride (Fig. 2*a*). Ideally, such curves should provide a method of estimating the chain length (cf. the thermal decomposition of ethers in the presence of nitric oxide, Hinshelwood and Staveley, *Proc. Roy. Soc.*, *A*, 1947, **159**, 192), providing that the reaction leading to inhibition is known with certainty. Failing such data, an approximate calculation gives an indication of the minimum number of carbon monoxide molecules which can suffer oxidation owing to the presence of one water molecule. It is assumed that the phosphorus halides function as inhibitors principally by virtue of their ability to react with water and oxygen to give metaphosphoric acid according to the equation

$$2POCl_3 + H_2O + 1\tfrac{1}{2}O_2 \longrightarrow 2HPO_3 + 3Cl_2.$$

The use of the data in Fig. 2*a* then suggests that the presence of one water molecule can lead to the oxidation of at least 500 carbon monoxide molecules. This latter figure is a lower limit because the calculation assumes that the *whole* of the phosphoryl chloride passed into the carbon tube reacts with water as indicated by the above equation. In point of fact, it is very unlikely that the water content of the gas phase was higher than 0·1%.

(iv) The above experiments indicate that species such as H_2O, H_2, H, OH, and perhaps O are involved in the reaction mechanism leading to carbon dioxide formation. These are not only highly reactive because of their chemical nature : their diffusion rates, especially those of H_2 and H, are large compared with that of O_2 :

$$O_2 : H_2O : OH : O : H_2 : H = 1 : 1{\cdot}33 : 1{\cdot}37 : 1{\cdot}4 : 4 : 5{\cdot}6.$$

Since burning rates in solid-fuel systems at high temperatures appear to be limited by diffusion or mass-transfer effects, the presence of the above materials is likely to be very significant. Moreover, some of the reactions leading to the secondary-heat release may be influenced by the hot fuel surfaces and the impurities that the latter contain. A link with the reactivity of solid fuels may be found here : the susceptibility of the water-gas reaction to catalysis by fuel surfaces is relevant in this connection.

(v) The fire-extinguishing properties of halogen-substituted hydrocarbons have generally been associated with their marked " shielding " effect against oxygen which arises from their relatively high density compared with oxygen. It has been suggested several times, however (Dufraisse and Horclois, *Compt. rend.*, 1931, **192**, 564; Bangham, *Trans. Faraday Soc.*, 1946, **42**, 376), that there is a specific retarding influence on the combustion. Since the above experiments prove that a gas phase reaction between carbon monoxide and oxygen certainly plays an important part during the combustion of solid fuels, a major part of the fire-extinguishing properties of halogen compounds must be ascribed to an inhibition of the combustion of carbon monoxide by species such as elementary halogen which can combine with the chain links. That so many fire-extinguishing agents contain halogen is significant not only on account of the shielding effect arising from high density but also because their electronegative pyrolytic products suppress the concentrations of chain links (*e.g.* H_2 and H). It should be noted that the change $CO + \frac{1}{2}O_2 \longrightarrow CO_2$ liberates about 2½ times as much heat as $C + \frac{1}{2}O_2 \longrightarrow CO$.

(vi) These experiments used relatively simple solid fuels. Commercial fuels such as coal clearly present additional complications. Nevertheless, the results represent the beginnings of a topochemical picture which is likely to be applicable to a stage of the combustion process of all solid fuels. Differences observed in the overall process due to superposition or otherwise of the various stages (Crone, *Coal Research,* March, 1945, 85, and in discussions with the authors) necessitate further experiments to identify the relevant stage with certainty.

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