87.   *The Slow Combustion of Acetylene.*

By ROBERT SPENCE.

ALTHOUGH it has long been suspected that the slow oxidation of hydrocarbons proceeds by a chain mechanism, it has not been possible until recently to reach any definite conclusions on this subject.   In the case of ethylene and oxygen, Spence and Taylor (*J. Amer. Chem. Soc.*, 1930, **52**, 2399) showed that introduction of ozone into the gas mixture caused additional amounts of oxygen to react, indicating the operation of a chain mechanism.   Later, Kistiakowsky and Lenher (*ibid.*, p. 3785) found that the kinetics of the acetylene–oxygen reaction were more consistent with a chain mechanism than with a simple mechanism.   A more detailed investigation of the same reaction was undertaken by Spence and Kistiakowsky (*ibid.*, p. 4837).   An apparatus was designed, in which any desired amounts of the gases could be circulated through a furnace at a given temperature, and the condensable products separated in a trap at $-78°$.   The diminution in total pressure was approximately equal to the amount of acetylene reacting, so the reaction rate could be followed manometrically and the initial rate for a large number of different mixtures determined.   After an experiment, liquid and gaseous products were analysed.   It was found that the rate is accelerated by oxygen when acetylene is in excess of the optimum mixture ($1\cdot4C_2H_2 + O_2$), but is retarded by it when oxygen is in excess.   At the optimum oxygen concentration the rate is proportional to the square of the acetylene concentration, while when less oxygen is present it is proportional to a lower power of acetylene concentration.   Under the conditions studied, the reaction exhibits an induction period of about 25 secs.   By using an improved form of apparatus, in which gas analyses could be carried out by the Bone and Wheeler method, the investigation has been extended to conditions of variable surface, very large excess of oxygen, etc.

Influence of Surface upon the Reaction Velocity.—Kinetic measurements at high rates of flow of gas through the furnace, such as experiments within the induction period require, cannot be given a

quantitative interpretation owing to the operation of undetermined mechanical factors on the rate of diffusion in the gas, and therefore on the reaction rate. For this reason, experiments in a static system are to be preferred. However, important deductions of a qualitative nature can be made from the results of the circulating experiments summarised in Table I, in which " dx/dt, corr." is the rate of pressure change (in mm. per 10 mins.) corrected to 98 c.c. volume. The volume per unit surface of furnace is given in column 5, and the time during which a given volume of gas was in contact with the furnace is recorded in column 6.

TABLE I.

Experiments at 320° in the induction period.

No.	C_2H_2, mm.	O_2, mm.	Vol. of furnace, c.c.	C.c./cm.² × 10².	Contact time, secs.	dx/dt.	dx/dt, corr.
1	175·8	172·3	98	68	27	5·9	5·9
2	183·1	171·8	98	68	14	5·6	5·6
3	179·8	176·5	98	68	8	4·4	4·4
4	188·4	191·9	27	45	12	2·0	6·2
5	193·6	194·8	27	45	2	1·6	5·0
6	192·2	188·8	27	45	2	1·8	5·6

Now, it appears from the work of Semenoff (*Z. physikal. Chem.*, 1931, *B*, **11**, 464), that in chain reactions the length of the induction period will vary with the initial number of active centres supplied per unit volume. Therefore, if the slow oxidation of acetylene is a chain reaction in which active centres originate at the surface, an increase in the relative amount of surface should be accompanied by a shorter induction period, and it is apparent from Table I that this is actually the case. The velocity after the induction period is also greater with greater surface, as would be expected if active centres originate at the surface. The results do not rule out the possibility of some initial homogeneous activation, but they do indicate that surface activation preponderates. If the two series of results in Table I are plotted, the time in which a given velocity of reaction within the induction period is attained can be determined approximately in each case. Substituting the values in Semenoff's equation (2) (Semenoff, *loc. cit.*), we can obtain an approximate value for $(\alpha - 1)\tau$, *viz.*, 0·4. (α is the mean number of active centres which every intermediate product forms as a result of passing into the end product; τ is the mean life of the intermediate product.) This compares with the value 0·02 which Semenoff (*loc. cit.*) derived from a consideration of Fort and Hinshelwood's results on methane and oxygen (*Proc. Roy. Soc.*, 1930, **129**, *A*, 284). Since $(\alpha - 1)/\tau$ is positive, it is to be concluded that the chains are branched, at least within the induction period. In a static system, of course, the value of $(\alpha - 1)/\tau$ would progressively decrease and finally become

negative just as in the case of methane (Semenoff, *loc. cit.*). α is the sum of two probabilities, *viz.*, (i) that of one more active centre being formed from each intermediate product molecule, and (ii) that of a second active centre arising during this process (see Bursian and Sorokin, *Z. physikal. Chem.*, 1931, *B*, **12**, 247), and one or both of these probabilities must decrease during the course of the reaction, otherwise the chain would become infinite and explosion would ensue.

In addition to its rôle as a positive catalyst, the surface can exert a very strong inhibitory effect. Table II shows the influence of decreasing average internal diameter of reaction vessel upon the velocity. The data apply to reaction vessels of volume 75 c.c., a temperature of 320°, and a contact period of 27 secs. (*i.e.*, greater than the induction period).

TABLE II.

Inhibition by the surface.

No.	C_2H_2, mm.	O_2, mm.	C.c./cm.^{2} $\times$ 10^2.	Approx. diam., mm.	G.-mols. of C_2 consumed, $\times$ 10^3.
1	269·4	145·4	5·5	2	0·3
2	268·4	147·1	5·5	2	0·1
3	269·1	145·4	5·5	2	0·1
4	269·8	146·7	9·5	4	0·1(5)
5	269·3	148·6	14·9	6	3·3
6	268·1	146·8	31·3	10	2·3
7	276·6	147·2	55·6	20	3·8

Expts. 1, 2, 3, and 4 were in vessels packed with Pyrex tubing of the internal diameter given under col. 5, and the volume/surface ratio (col. 4) takes into account the total surface exposed. Expts. 5 and 6 were in vessels of coiled Pyrex tubing having the internal diameter given, and a plain cylindrical furnace was used in expt. 7. Although other conditions in the various reaction vessels were evidently not perfectly uniform, the results nevertheless indicate that under the conditions of temperature and concentration stated, in reaction vessels of less than 4 mm. internal diameter, acetylene and oxygen react very slowly, but in vessels greater than 6 mm. internal diameter, the reaction proceeds at what may be considered its normal rapid rate. Critical diameters below which the rapid reaction does not occur have been observed in the explosive combustion of other hydrocarbons. Davy ("Collected Works," **6**, 11) found that mixtures of firedamp and air could not be fired in tubes of 1/7 inch diameter; Mallard and Le Chatelier (*Ann. Mines*, 1883, viii, **4**, 319) observed that no explosion of methane occurred in tubes of 3·2 mm. diameter, while Payman and Wheeler (J., 1918, **113**, 656) found 3·6 mm. to be the critical diameter for methane. It is evident from what has been said in respect of Table I, that the

velocities recorded in Table II show the operation of two effects :
(1) variation of reaction rate directly with extent of surface, and (2)
inhibition by the surface.   The concept of branched chains utilised
to explain the results contained in Table I offers the readiest explan-
ation of this surface inhibition.   It being assumed that the reaction
in packed vessels represents the initial rate of supply of active centres,
or the number of chains started, the chain length in the wide vessel
is 380 (after correction to unit surface).   This figure represents the
minimum number of acetylene molecules oxidised as a result of one
initial activation, although the actual figure may be many times
greater.

The well-known inhibitory effect of potassium chloride in hydro-
carbon oxidations (Pease, *J. Amer. Chem. Soc.*, 1929, **51**, 1839) can
be observed in the slow oxidation of acetylene.   In Table III the
results of experiments in a reaction vessel of 25 mm. diameter and
98 c.c. volume at 320° are given.   A surface of potassium chloride
was formed by rinsing the vessels with a 20% solution of the salt.

TABLE III.

Specific wall effect.

C_2H_2, mm.	O_2, mm.	Wall.	dx/dt.
264·7	134·6	Glass	10·3
264·4	136·6	Glass	10·6
266·4	141·3	KCl	3·5
264·8	141·8	KCl	3·6

Experiments in which a potassium chloride-coated wall was used
gave slower rates of reaction than those in the plain glass vessels.
As the diameter of the reaction vessel was much greater than the
critical diameter (less than 4 mm.) at which surface inhibition
becomes prominent, one can only ascribe such a considerable diminu-
tion in the reaction rate with saline walls to a smaller efficiency on
the part of the salt in catalysing the production of active centres.
This view of the behaviour of potassium chloride has been discussed
in its broader aspects by H. S. Taylor (*Chem. Reviews*, 1931, **9**, 20).
Other substances, particularly potassium silicate, have a more
pronounced effect in the case of ethylene (Lenher, *J. Amer. Chem.
Soc.*, 1931, **53**, 3744).   On the other hand, the results (Table II) do
not decide whether there is any specific difference in the inhibitory
effects of different substances, but if such differences do exist, one
would expect to find a variation in the critical diameter with the
nature of the wall.

Analysis of the Reaction Products.—The gaseous products of reac-
tion were analysed in a Bone and Wheeler gas analysis apparatus,
and the condensable products were determined by the methods

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previously described (Spence and Kistiakowsky, *loc. cit.*), *viz.*, precipitation of the aldehydes with *p*-nitrophenylhydrazine and separation of the formaldehyde hydrazone by extraction with chloroform. Titration of the formic acid must be performed in the presence of an indicator changing on the acid side, such as bromo-cresol-purple, because if the solution becomes alkaline, glyoxal is titrated as glycollic acid (Greenwald, *J. Biol. Chem.*, 1918, **35**, 472). It was observed, however, that even in the presence of phenol-phthalein a permanent end-point could not be attained, but that after the solution had been boiled, a further small addition of alkali was necessary. This property of delayed titration is characteristic of the glycerosone obtained by Norrish and Griffiths (J., 1928, 2829) from the photochemical decomposition of glyoxal,

$$2(CHO)_2 \longrightarrow CO + CHO \cdot CO \cdot CH_2OH.$$
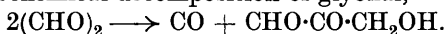
The aqueous solution of the condensate also reduces Fehling's solution in the cold, a reaction which is not given by formic acid, formaldehyde, or monomeric glyoxal, but is characteristic of glycerosone (Norrish and Griffiths, *loc. cit.*). However, this test is also given by trimeric glyoxal (Harries and Temme, *Ber.*, 1907, **40**, 165). An attempt to separate the *p*-nitrophenylhydrazone of this substance from the chloroform extract yielded only a trace of material of undetermined character, melting at 260° after recrystallis-ation from toluene. In consideration of its relatively small con-centration, the glycerosone was neglected in the analyses. Table IV gives the amounts of products formed (in g.-atoms $\times$ 10^{-3}) of carbon, oxygen, and hydrogen.

TABLE IV.

Carbon balance.

No.	C_2H_2, in.	C_2H_2, out.	C_2H_2 used.	CO.	CO_2.	$(CHO)_2$.	CH_2O.	$H \cdot CO_2H$.
1	20·2	16·4	3·8	1·6	0·4	0·67	0·34	0·22
2	19·6	17·3	2·3	1·0	0·3	0·45	0·11	0·12
3	19·6	16·3	3·3	1·5	0·45	0·70	0·16	0·08

Oxygen balance.

No.	O_2, in.	O_2, out.	O_2 used.	In products.	$H_2O(?)$.
1	10·7	6·0	4·7	3·85	0·85
2	10·7	7·7	3·0	2·40	0·60
3	10·8	6·5	4·3	3·42	0·88

Hydrogen balance.

No.	H_2 used.	H_2 freed.	In products.	$H_2O(?)$.
1	3·8	0·2	1·79	1·81
2	2·3	0·1	0·90	1·30
3	3·3	0·15	1·18	1·97

Experiments were carried out at 320°, and for expt. 1 a 20-mm.

diameter reaction vessel was used; for 2, a 10-mm. vessel; and for 3 one of 6-mm. diameter.

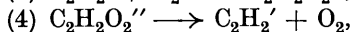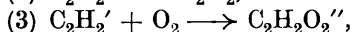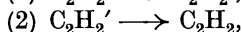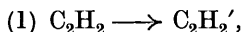*Kinetics of the Reaction.*—The mechanism advanced by Bodenstein (*Z. physikal. Chem.*, 1931, *B*, **12**, 151), although in good agreement with the majority of the kinetic results, is unsatisfactory for the following reasons : (1) with initial pressures of acetylene below 100 mm., the formula gives a low value of k (Table V); (2) reactions (5) and (6) of the mechanism, *viz.*,

(5) $C_2H_2O_2' + O_2 \longrightarrow CO_2 + H \cdot CO_2H$,
(6) $C_2H_2O_2' \longrightarrow CO + H \cdot CHO$,
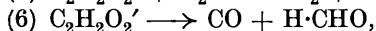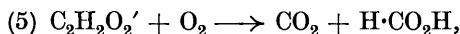
do not account for the proportions in which carbon monoxide and dioxide, formaldehyde, and formic acid are formed (Table IV), since formaldehyde (Askey, *J. Amer. Chem. Soc.*, 1930, **52**, 974) and formic acid (Fort and Hinshelwood, *Proc. Roy. Soc.*, 1930, **129**, *A*, 287) are perfectly stable at 320° in the short contact period used; (3) the mechanism does not allow of the possibility of branching chains. To account for these discrepancies and for the fact that carbon dioxide cannot arise from the decomposition of formic acid, the mechanism has been modified as follows :

(1) $C_2H_2 \longrightarrow C_2H_2'$,
(2) $C_2H_2' \longrightarrow C_2H_2$,
(3) $C_2H_2' + O_2 \longrightarrow C_2H_2O_2''$,
(4) $C_2H_2O_2'' \longrightarrow C_2H_2' + O_2$,
(5) $C_2H_2O_2'' + C_2H_2 \longrightarrow C_2H_2' + C_2H_2O_2'$,
(6) $C_2H_2O_2' + C_2H_2 \longrightarrow C_2H_2' + C_2H_2O_2$,
(7) $C_2H_2O_2'' + O_2 \longrightarrow 2CO + H_2O_2$,
(8) $C_2H_2O_2' + O_2 \longrightarrow CO + CO_2 + H_2O$,
(9) $C_2H_2O_2' \longrightarrow CO + H \cdot CHO$,
(10) $2C_2H_2O_2' \longrightarrow CO + CHO \cdot CO \cdot CH_2OH$.
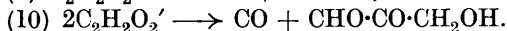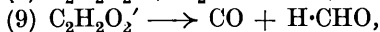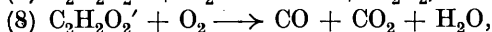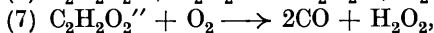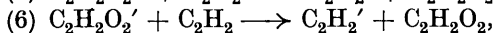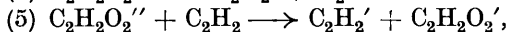
The intermediate product is assumed to exist in two forms, $C_2H_2O_2''$ and $C_2H_2O_2'$, which represent different energy levels in the system $C_2H_2O_2$, and whose successive degradation to glyoxal introduces the possibility of branched chains. It is also assumed that glyoxal, like all the other end products, is stable under the conditions of the experiment. That the mechanism is in agreement with the ratio of the products appears from a consideration of expt. 1, Table IV. We can assume that all the formic acid comes from formaldehyde by oxidation with hydrogen peroxide (see Lenher's results on ethylene, discussed below), giving 0·54 unit of carbon as formaldehyde and therefore 0·54 unit of carbon monoxide by reaction (9); 0·4 unit of carbon dioxide appears by reaction (8), and hence 0·4 unit of carbon monoxide. If all the peroxide is measured

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in the acid titration, 0·44 unit of carbon monoxide appears by reaction (7). We have then :

CO from reaction (7) 0·44 unit. ⎫ Total, 1·38 units.
CO from reaction (8) 0·40   ,,   ⎬ Found (by analysis),
CO from reaction (9) 0·54   ,,   ⎭ 1·60 units.

Some of the excess monoxide may come from reaction (10). The tables show about 0·4 unit of carbon unaccounted for. This may be due to some constant error in estimation or may be partly due to the glycerosone. The value for water is also slightly higher than would be expected from reactions (7) and (8), possibly owing to the same reason.

If it is assumed that in the denominator a negative term, viz., $\dfrac{[C_2H_2]^2[O_2]k_3k_5k_6}{[C_2H_2]k_6 + [O_2]k_8 + k_9}$, is small in comparison with the positive terms (for division throughout by $[C_2H_2]k_6$, which is approximately equal to $[O_2]k_8$, gives as an approximation $[C_2H_2][O_2]k_3k_5/2$, which can be assumed to be of negligible importance compared with the other terms in the denominator), reactions (1) to (9) then lead to the equation

$$-\frac{d[C_2H_2]}{dt} = k_1 \frac{[C_2H_2][O_2](k_5[C_2H_2]/k_7 + [O_2])}{[O_2]^2 + k_2k_4/k_3k_7}.$$

According to expt. 1, Table IV, the ratio

$$\frac{k_5}{k_7} = \frac{(0·67 + 0·80 + 0·68)[O_2]}{0·44[C_2H_2]} = \frac{2·15 \times 147}{0·44 \times 276} = 2·6.$$

Giving the denominator constant a value of 4000, instead of 2000 as in Bodenstein's equation, we have

$$-\frac{d[C_2H_2]}{dt} = k_1 \frac{[C_2H_2][O_2](2·6[C_2H_2] + [O_2])}{[O_2]^2 + 4000}.$$

Results of a further series of experiments at 90 and 50 mm. of acetylene and with very large excess of oxygen are given in Table V, together with previous results of Spence and Kistiakowsky (loc. cit.). The values of k_1 derived from the above equation are better at low concentrations of acetylene than those of k given by Bodenstein's equation.

In most cases the variation of the constant k_1 from a mean value of 9 does not appear to be greater than the experimental error. Therefore, besides furnishing an explanation of the influence of surface on the induction period, etc., the concept of branched chains affords a ready explanation of the reaction kinetics.

TABLE V.

Variation of rate with concentration of reactants.

C_2H_2, mm.	O_2, mm.	dx/dt.	k.	k_1.	C_2H_2, mm.	O_2, mm.	dx/dt.	k.	k_1.
50	101	0·09		10	175	87	0·66	15	9
50	500	0·05		8		192	0·56	15	11
60	21	0·06	9	12		264	0·53	16	12
70	46	0·11	9	9		304	0·48	15	12
70	75	0·10	8	7		349	0·42	14	11
60	88	0·07	6	6	260	8·5	0·60	16	16
60	174	0·05	3	5		19	0·78	11	10
90	94	0·18		9		27	1·00	12	10
	177	0·14		8		90	1·08	12	7
	267	0·09		6		175	1·16	16	13
	360	0·08		6	345	9·5	0·66	8	9
	450	0·09		7		17	1·34	13	10
175	18	0·50	16	15		27	1·28	10	7
	27	0·54	14	11		45	1·72	12	7
	44	0·64	15	10		73	1·80	12	7
	70	0·64	14	9		87	2·00	14	8
						129	2·04	16	9

Discussion.

Although the above conclusions can only apply strictly to the conditions studied, yet they contain in essence the explanation of many scattered and apparently conflicting facts concerning hydrocarbon oxidation. Lenher (*J. Amer. Chem. Soc.*, 1931, 53, 2962) has shown that the acetylene–oxygen reaction can be catalysed by the oxides of nitrogen. At 260° the chief product is trimeric glyoxal, less than 3% of the acetylene used going to formaldehyde and formic acid. Presumably, the oxides of nitrogen start the chain just as ozone does in the case of ethylene (Spence and Taylor, *loc. cit.*), but at the comparatively low temperature of reaction, deactivating collisions between the intermediate product and oxygen lead to the formation of stable glyoxal rather than to the oxides of carbon. Nevertheless, owing to the stability of formaldehyde and formic acid at 260°, the small quantities of carbon dioxide and water that are formed must be due to the limited operation of reactions (7) and (8). Also Mardles (*Trans. Faraday Soc.*, 1931, 27, 718) has shown that metal surfaces, carbon disulphide, and lead tetraethyl inhibit the reaction. This is probably due to the breaking of chains by deactivating collisions with the intermediate product.

The experiments of Lenher (*J. Amer. Chem. Soc.*, 1931, 53, 3737) on the slow oxidation of ethylene show a close parallelism between this reaction and acetylene. The reaction has an induction period, is very strongly inhibited in packed vessels, and in open vessels the rate is determined by the nature of the wall. Thompson and Hinshelwood (*Proc. Roy. Soc.*, 1929, 125, A, 277) have shown that the rate of oxidation of ethylene is approximately proportional to the square of ethylene concentration. This has been confirmed by

Lenher (*loc. cit.*), whose results also indicate that the variation of reaction rate with oxygen concentration is similar to that observed with acetylene.   The following results at 390° are taken from Tables I and II of Lenher's paper, the concentrations being given in mm. pressure instead of percentage : 360 c.c. of gas were passed through a furnace of 65 c.c. volume and 20 mm. diameter with a contact period of 75 secs.
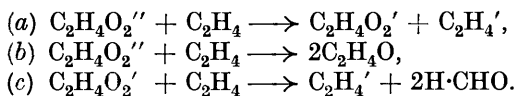
TABLE VI.

Influence of oxygen concentration on the rate of oxidation of ethylene
(calculated from Lenher's data).

	Initial concentrations.		Products.	
No.	C_2H_4, mm.	O_2, mm.	Condensable matter, g.	CO, c.c.
1	380	80	0·0485	18·5
2	380	80	0·0530	23·8
3	380	380	0·1342	74·1
4	380	380	0·1341	67·9
5	190	570	0·0142 (0·0568)	4·6 (18·4)
6	190	570	0·0162 (0·0648)	7·5 (30·0)

The oxygen in expts. 1 and 2 was supplied as air, but Thompson and Hinshelwood (*loc. cit.*) have shown that nitrogen has very little influence on the rate of reaction.   For purposes of comparison, the results of expts. 5 and 6 are corrected by the square law to 380 mm. of ethylene, the corrected values being given in parentheses.   It is clear that there is, just as in the case of acetylene, an increase of rate with oxygen concentration to a maximum close to the equimolecular mixture, after which further increase of oxygen reduces the rate to about half its maximum value.   These kinetic characteristics lead one to expect a reaction mechanism similar to that of the acetylene-oxygen reaction.   Lenher (*loc. cit.*) has definitely established the presence of hydrogen peroxide in the products of slow oxidation of ethylene, and shown that it must be produced in considerable quantity by the isolation of dihydroxymethyl peroxide, the product of its condensation with formaldehyde.   The origin of hydrogen peroxide has been attributed by Lenher to a reaction between steam and the collision complex, but in view of the small concentration of these reactants such a process would not be expected to occur with sufficient frequency to account for the amount of hydrogen peroxide produced.   A much more probable source of the hydrogen peroxide would be a deactivating collision with oxygen similar to reaction (7) in the acetylene mechanism.

The induction period and wall effect undoubtedly point to the presence of branched chains of considerable length under favourable conditions of concentration and diameter of vessel.   However, with an initial ratio of $8·5C_2H_4 : 1·5O_2$ at 365°, Lenher obtained 13·7% of the ethylene consumed in the form of ethylene oxide.   Also, at 435°

with an initial ratio of $8 \cdot 0C_2H_4 : 1O_2$, $21 \cdot 27\%$ of ethylene oxide and $13 \cdot 53\%$ of acetaldehyde were recovered from 100% of ethylene used. It seems very probable, as Lenher suggests, that ethylene oxide arises from a collision between an ethylene molecule and the primary collision complex, but these results are not sufficient ground for the assumption that ethylene oxide is the principal primary product of the reaction and consequently that the chain length cannot be greater than 2 (Lenher, *J. Amer. Chem. Soc.*, 1931, **53**, 3763). The experiments quoted above were performed at relatively high temperatures and under conditions where the probability of the intermediate compound colliding with an ethylene molecule would be eight times greater than its probability of collision with an oxygen molecule. The comparatively high concentration of excited ethylene molecules produced in these circumstances is shown by the considerable degree of polymerisation in Lenher's experiments at 485°. We have, therefore, to assume some such deactivating collisions with ethylene as the following :

(a) $C_2H_4O_2'' + C_2H_4 \longrightarrow C_2H_4O_2' + C_2H_4'$,

(b) $C_2H_4O_2'' + C_2H_4 \longrightarrow 2C_2H_4O$,

(c) $C_2H_4O_2' + C_2H_4 \longrightarrow C_2H_4' + 2H \cdot CHO$.

In the experiment under consideration $(8 \cdot 0C_2H_4 : 1O_2$ at 435°), $47 \cdot 1\%$ of formaldehyde was formed, indicating the continuance of a reaction chain supplying active centres, despite the deactivation of its branches by reactions such as (b) above. Deactivation by oxygen is measured approximately by the amount of carbon monoxide produced (less than $12 \cdot 3\%$). The evidence in respect of this particular phase of the reaction is therefore perfectly consistent with its branching-chain character, and ethylene oxide cannot be regarded as an essential intermediate step but is the result of one of several alternative deactivating processes whose individual importances are determined by the conditions of experiment. The production of methyl alcohol from methane, quoted by Bone (*Nature*, 1931, **127**, 481) as evidence in favour of his " hydroxylation theory " of combustion, is to be accounted for in a similar manner.

Summary.

The slow oxidation of acetylene proceeds by a branched-chain mechanism.

At 320° wall activation is predominant.

At 320° and 400 mm. total pressure, the reaction is almost completely inhibited by the walls in vessels of less than 4 mm. diameter.

In vessels greater than 6 mm. diameter, inhibition by the wall is small compared with inhibition by oxygen.

A modification of the mechanism proposed by Bodenstein accounts for all the kinetic phenomena.

It is shown that the slow oxidation of ethylene proceeds by a similar mechanism.