$Cd(Hg) \mid CdCl_2{\cdot}2.5H_2O\ (sat.) \mid CdCl_2{\cdot}2.5H_2O\ (sat.),\ PbCl_2 \mid Pb(Hg)$ (1)
$Cd(Hg) \mid CdCl_2{\cdot}2.5H_2O\ (sat.) \mid CdCl_2{\cdot}2.5H_2O\ (sat.),\ Hg_2Cl_2 \mid Hg$ (2)
$Pb(Hg) \mid PbCl_2\ (sat.) \mid PbCl_2\ (sat.),\ Hg_2Cl_2 \mid Hg$ (3)

When hemipentahydrated cadmium chloride was the solid salt in equilibrium with the electrolyte in Cell 1, the values were in good agreement with the values found by Obata. When monohydrated cadmium chloride was the solid salt in equilibrium (or metastable equilibrium) with the electrolyte, the values were in good agreement with those found by Vosburgh when his cells had the monohydrate as the solid phase.

A value only slightly lower than that of Lipscomb and Hulett was found for Cell 2.

From the values for Cells 1 and 2 a value for Cell 3 was calculated which agreed with the observed values for Cell 3 and with Gerke's values for this cell. Of the three this cell was the most difficult to reproduce.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

KINETICS OF THE ACETYLENE–OXYGEN REACTION

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Although of extraordinary technical and general interest, the problem of the mechanism of hydrocarbon combustion has yielded very little exact, reproducible information despite numerous investigations, principally owing to the complexity of the process and the consequent possibility of considerable variation in the course of reaction with changing conditions. However, the results of more recent experimental work on the slow oxidations of gaseous hydrocarbons have led several workers to postulate a chain mechanism.[1] Thus, it was found that in vessels packed with pieces of the same material as that of the containing walls, the reaction velocity is slower and the products are, in general, somewhat different. An even more direct evidence in favor of this hypothesis has been obtained by Spence and Taylor,[2] who showed that small amounts of ozone introduced into a stream of slowly reacting oxygen and ethylene accelerate the rate of reaction between the latter. In the few cases that have been studied, the reaction kinetics appear to be somewhat unusual and favor the assumption of a chain mechanism. Thompson and Hinshelwood[1] observed that the velocity of the ethylene–oxygen reaction is proportional to a high power of ethylene concentration and is almost independent of oxygen. Very similar

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[1] Pease, THIS JOURNAL, **51**, 1839 (1929); Pope, Dykstra and Edgar, *ibid.*, **51**, 2203, 2213 (1929); Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **125A**, 277 (1929); Kistiakowsky and Lenher, *Nature*, **124**, 761 (1929); THIS JOURNAL, **52**, 3785 (1930).

[2] Spence and Taylor, *ibid.*, **52**, 2399 (1930).

observations have been made with acetylene,[3] hydrogen,[4] higher aliphatic hydrocarbons,[5] and benzene.[6] Hence, it appears that many gaseous hydrocarbon oxidation reactions have common properties and therefore anything which is found true for one of them may very probably apply to other hydrocarbons with little modification.

Since the complexity of the oxidation reaction undoubtedly increases with the size of the hydrocarbon molecule, the authors decided to study the oxidation of that one having the smallest number of atoms, namely, acetylene, which reacts with oxygen at moderate temperatures and thus makes the isolation of unstable intermediary products more probable. Those who have studied this reaction previously employed two methods of attack. Bone and Andrew[3] enclosed various mixtures of oxygen and acetylene at known total pressures in glass bulbs, raised the bulbs to given temperatures for a certain time, then noted the pressure change after cooling to room temperature and finally analyzed samples of the gases. The principal gaseous product was carbon monoxide. In a second series of experiments they employed a flow system, but in this case their reaction vessel was packed with broken porcelain and the gaseous product contained a much larger percentage of carbon dioxide. The work of Kistiakowsky and Lenher[1] on flowing mixtures of acetylene and oxygen showed that Bone and Andrew's bulb reactions were of the homogeneous kind, while the packed tube reactions giving a larger proportion of carbon dioxide were principally of the wall variety. The authors decided to use a circulating system for their experiments because it combines the advantages of the previous static and flow methods. In the apparatus finally adopted, gases could be admitted in any given amounts up to atmospheric pressure, could be circulated through the furnace at a given rate and the total pressure in the apparatus noted at intervals. A U-tube cooled in carbon dioxide and ether removed all condensible products immediately on leaving the furnace and these could be analyzed after the experiment, together with a sample of the gaseous products.

Circulating Pump.—Mixtures of acetylene and oxygen are extremely sensitive and will explode with great violence on the slightest provocation. A circulating pump necessitates considerable friction, particularly in valves, with the consequent possibility of electrical discharges. In the first apparatus the circulating pump was equipped with mercury non-return valves but these would detonate the gas mixture without warning after working satisfactorily for as many as six experiments. Then an all-glass valve was evolved, similar in design to that shown in Fig. 1. A

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[3] Kistiakowsky and Lenher, Ref. 1; Bone and Andrew, *J. Chem. Soc.*, **87**, 1232 (1905).

[4] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **122**, 615 (1929).

[5] Lewis, *J. Chem. Soc.*, 58 (1930).

[6] Fort and Hinshelwood, *Proc. Roy. Soc.* (London), **127A**, 218 (1930).

flexible glass plate, no more than 0.002 in. thick was held against the flat, ground end of a capillary tube by a fine glass rod sealed into a side tube. A non-return valve of this type is efficient, sturdy and simple to make. However, despite the fact that practically all mechanical friction had been eliminated, explosions still resulted. Here the source of the trouble seemed to be the "Armstrong effect" of dry gases streaming from a narrow jet, giving an electrical charge to the jet which eventually discharged to the glass plate, the latter having meanwhile taken the opposite charge from the gases. In the design eventually adopted, and which proved to be quite successful (Fig. 1), the tip of the capillary jet was coated with a mirror of platinum and the glass plate replaced by a thin plate of beaten platinum foil welded to a tungsten wire sealed into the side tube. The end of the tungsten wire was connected to earth and all possibility of an accumulation of electrical charge removed. While not so efficient as the glass or mercury valves the new type allowed of a reasonable rate of pumping, which was all that was required. Attempts were made to localize explosions in order to prevent complete destruction of the apparatus which inevitably ensued when all the gas mixture was detonated. Tubes containing fairly tight wads of cotton wool placed at either end of the circulating pump proved to be very efficient and while they were in use no explosion spread beyond the valves of the circulating pump. Fig. 1 illustrates the arrangement of the circulating pump. Four valves were connected to the steel pump barrel by two glass tubes longer than a barometric column. These columns were filled with mercury which could be given an oscillating motion by movement of the piston in the steel cylinder. A packing composed of a mixture of stopcock grease, asbestos pulp and graphite, enclosed in the piston gland, effectively prevented any leakage of mercury, while cheesecloth filters placed at the foot of the mercury columns helped to keep the mercury free from grease contamination.

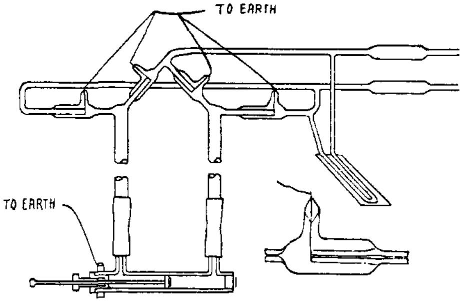

Fig. 1.—Circulating pump and valve.

Main Apparatus.—By far the larger part of the total gas enclosed in the apparatus was contained in two glass bulbs, each of 200 cc. capacity, placed next to the pump. A large very stout wooden cover surrounded the bulbs, which were connected to the cotton wool safety tubes on either end of the pump. The gases could be circulated around the pump and bulbs to ensure thorough mixing, then admitted to the furnace circuit which had previously been evacuated. The furnace consisted of a pyrex glass tube of 98 cc. capacity into which was sealed a tube containing a thermocouple. Immediately on leaving the furnace, the gases passed into a U-tube cooled in a carbon dioxide–ether mixture and which was connected to the apparatus by two ground-glass joints sealed with piceine wax. To ensure uniformity of conditions before and after the reaction, another U-tube cooled in carbon dioxide–ether mixture was placed immediately before the furnace, while the pressure of the gases entering this U-tube was measured on a mercury manometer having a barometer attached to the same scale.

Purification of the Gases.—Oxygen from a tank was dried in a sulfuric acid wash bottle, then passed into a storage bulb via a U-tube immersed in a solid carbon dioxide-ether mixture. Acetylene, obtained from a small Prestolite tank, was bubbled through water, a mixture of cupric and ferric chloride solutions, caustic potash and finally passed over calcium chloride into a vessel cooled in liquid air, where it condensed to a white solid. Inert gases were removed by evacuation, the solid was distilled from a carbon dioxide–ether bath and the middle fraction collected in a storage bulb. After further solidification and evacuation, the acetylene was again allowed to evaporate into the bulb, where it was ready for use.

Calibration of the Apparatus.—The volume of the apparatus and its parts was determined by admitting gas at known pressure and volume into the evacuated apparatus and reading the pressure.

Volume of circulating pump and capacity bulbs	550 cc.
Volume of furnace (cold)	98 cc.
Volume of U-tubes, etc.	26 cc.
Total volume	674 cc.

In order to know the time of contact of the gases with the furnace at the various pressures studied, the U-tube was replaced by two 500-cc. bulbs connected by a stout, wide bore, rubber tubing, containing a strong solution of calcium chloride. The time necessary to transfer 500 cc. of liquid (the levels of the solution in the two bulbs being kept the same) was noted over a large range of pressures and pumping rates and the results were plotted so that the contact period for any given conditions could easily be read off.

Experimental Method.—Before beginning an experiment, the furnace was adjusted to the required temperature, the U-tubes surrounded with carbon dioxide–ether mixtures, and the whole apparatus evacuated. After having shut off the furnace section from the rest of the apparatus, definite amounts of acetylene and oxygen, measured on the manometer, were admitted and circulated for about five minutes to ensure good mixing of the two gases. At this point the necesary stopcocks were turned, bringing the furnace into the circulating system and closing the by-pass. Readings of manometer, barometer, temperature and pumping rate were taken immediately and at given intervals thereafter until the experiment was finished. Upon completion of an experiment, the furnace was again shut off, evacuated, and a sample collected from the remaining gas by a mercury pipet in which it was retained for analysis.

Analysis of the Products.—At the end of an experiment, the U-tube contained a mixture of polymerized glyoxal, formaldehyde, formic acid and water. These were washed out with hot water, in which the polyglyoxal dissolves, a hot solution of the hydrochloride of *p*-nitrophenylhydrazine added and the mixture filtered through a tared Gooch crucible. After drying and weighing, the crucible was placed in a Soxhlet apparatus and extracted with chloroform. This treatment removed the *p*-nitrophenylhydrazone of formaldehyde and left the *p*-nitrophenylosazone of glyoxal behind. A final drying and weighing gave the weight of formaldehyde and glyoxal. The *p*-nitrophenylosazone of glyoxal crystallizes from pyridine in long red needles, m. p. 318°. *Anal.* Calcd. for $C_{14}H_{12}O_4N_6$: C, 51.2, H, 3.7. Found: C, 51.35, H. 3.9. In an identical experiment, the condensate was made up to 10 cc. and two 5-cc. portions were titrated with $N/100$ baryta solution, using brom cresol purple as indicator. This gave the amount of formic acid present. The gas collected over mercury was analyzed for acetylene (by fuming sulfuric acid), carbon dioxide, oxygen, carbon monoxide and hydrogen (over heated copper oxide). From these figures, a balance of carbon, before and after the reaction, could be made.

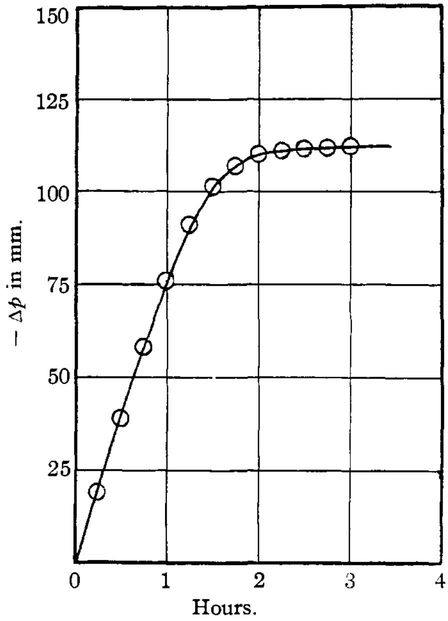

Fig. 2.—$-\Delta p$ curve for a mixture of approx. 400 mm. C_2H_2 and 100 mm. O_2 at 320°, reaction carried to completion.

Experimental Part

Figure 2 represents a typical experiment which has been carried to completion and shows the general form of the pressure-time curve. The example shown, however, was not obtained with an apparatus identical with that used in the principal experiments. The results of all the experiments quoted below were plotted in a similar manner and dx/dt, the initial rate of reaction in mm. per minute, obtained by direct measurement.

The Induction Period.—To ascertain the effect of varying rates of pumping on the reaction velocity, series of mixtures of constant composition were circulated at different rates and the reaction velocity determined.

Table I

Effect of Contact Time on Reaction Velocity

No.	C_2H_2, mm.	O_2, mm.	Contact time, sec.	dx/dt
32	175.7	192.6	50	0.56
33	173.7	191.3	12	.34
34	173.6	192.6	18	.44
35	173.4	191.4	37	.56

We see that for contact periods greater than about twenty-five seconds, the rate is independent of the pumping speed. The rapid falling off in reaction rate with higher pumping speeds must be due to the existence of an induction period.

Temperature Coefficient.—Measurements of rates of reaction of given mixtures at different temperatures are given in Table II. In all succeeding experiments the rate of pumping was arranged so as to give a constant contact period of about forty seconds.

In Fig. 3 are plotted the logarithms of the reaction velocity against the reciprocal of absolute temperature. Within the narrow temperature interval investigated, the experimental points lie on straight lines and the slope is independent of the composition of the gas mixture, but it is realized that more extended experiments may show a deviation from these results. From the observed temperature coefficient, the activation energy of the reaction is calculated to be 34,700 cal. at 320°.

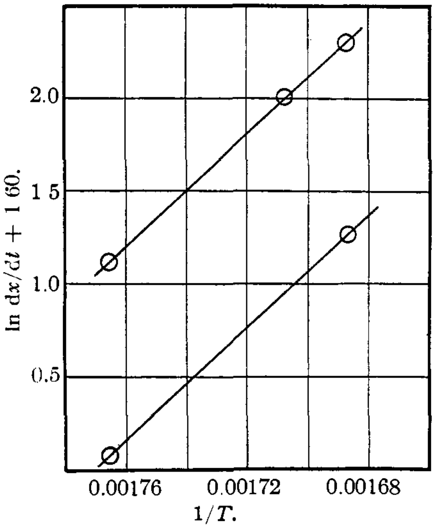

Fig. 3.—Logarithm of rate of reaction plotted against $^1/_{T_{\text{abs.}}}$ for two different mixtures.

Influence of Acetylene and Oxygen Concentrations.—Table III gives the initial concentrations of acetylene and oxygen, the pressure decrease at five-minute intervals and the initial rate as measured from each curve. The meaning of K_0 is explained below. All experiments were carried out at 320° with a contact period of forty seconds.

Plotting rate against oxygen concentration, we obtain the four curves

TABLE II

RATE OF REACTION AT DIFFERENT TEMPERATURES

No.	C_2H_2, mm.	O_2, mm.	T, °C.			Δp				
				5 min.	10	15	20	25	30	dx/dt
2	346.7	86.3	297.0	3.1	6.3	9.4	12.2	15.0	17.7	0.64
1	346.6	86.9	313.5	7.1	14.8	22.5	29.3	36.3	42.8	1.5
4	347.9	86.9	320.0	10.1	19.8	29.6	39.4	47.2	54.5	2.0
3	173.8	86.5	297.0	1.1	2.0	2.9	3.6	4.4	5.2	0.22
5	173.7	87.2	320.0	3.4	6.9	9.9	12.7	15.3	18.0	0.72

TABLE III

EXPERIMENTS AT 320°

No.	C_2H_2, mm.	O_2, mm.			Δp					
			5 min.	10	15	20	25	30	dx/dt	K_0
43	61.2	20.6	0.3	0.5	0.9	1.2	1.6	1.9	0.06	1.35
38	70.4	45.9	.5	1.1	1.7	2.2	2.8	3.3	.11	2.21
41	70.6	74.9	.5	1.0	1.6	2.3	2.6	3.1	.10	2.12
42	60.6	88.1	.3	0.7	1.1	1.6	2.1	2.6	.07	2.32
40	61.1	173.9	.2	.5	0.8	1.2	1.5	1.7	.05	2.12
15	174.6	8.5	2.5	4.2	5.8	6.6	7.1	7.4	.48	2.26
18	173.4	17.6	2.4	4.6	6.7	8.6	10.4	11.8	.50	1.68
20	176.7	26.5	2.3	5.1	8.1	11.0	13.5	15.6	.54	1.63
22	175.8	43.5	2.8	6.6	9.8	12.8	16.8	20.0	.64	1.93
30	173.2	70.3	3.3	6.5	9.7	12.7	16.0	19.3	.64	2.09
5	173.7	87.2	3.4	6.9	9.9	12.7	15.3	18.0	.72	2.34
26	172.7	87.3	3.3	6.5	9.4	12.6	14.7	17.0	.66	2.24
35	173.4	191.4	2.4	5.6	8.5	11.4	13.7	16.2	.56	2.15
32	175.7	192.6	2.5	5.6	8.3	11.1	13.5	16.1	.56	2.10
28	176.2	264.1	2.7	5.4	7.9	10.6	12.8	15.3	.53	2.15
29	175.4	303.5	2.4	4.9	7.2	9.4	11.6	14.1	.48	2.05
44	172.1	348.1	..	3.9	..	7.8	..	11.5	.40	1.85
25	173.4	350.1	2.2	4.2	6.4	8.3	10.3	12.2	.44	1.99
10	262.8	1.1	0.3	0.6	0.8	1.0	1.2	1.2	.05	2.88
9	262.3	8.5	2.8	5.1	6.9	8.1	8.9	9.2	.60	2.28
8	262.6	19.2	3.6	7.2	10.5	12.8	14.9	16.2	.78	1.38
6	260.3	26.5	4.3	9.1	13.3	16.5	19.4	22.0	1.00	1.56
11	259.5	90.1	5.2	10.6	16.2	21.3	27.0	33.0	1.08	1.54
12	260.8	175.0	5.3	10.9	17.1	21.9	29.3	32.9	1.16	1.80
16	345.5	9.5	3.2	5.6	7.4	8.5	9.4	9.8	0.66	1.92
17	347.5	17.4	5.9	10.9	14.3	16.5	18.2	19.2	1.34	1.91
19	348.0	26.8	5.5	11.5	15.6	18.9	21.9	23.5	1.28	1.32
21	346.3	44.7	8.5	16.7	24.5	30.6	35.4	37.9	1.72	1.48
23	350.8	72.6	7.5	18.0	27.0	34.8	41.8	46.8	1.80	1.43
4	347.9	86.9	10.1	19.8	29.6	39.4	47.2	54.5	2.00	1.61
36	357.0	129.0	..	20.5	..	40.0	..	58.4	2.04	1.58
37	329.0	13.10	..	18.9	..	36.2	..	52.4	1.86	1.70

shown in Fig. 4. In each case, increase in the oxygen concentration from zero causes an increase in the rate of reaction, until a region is reached where the rate is practically independent of oxygen. Further increase in oxygen concentration somewhat retards the rate of reaction, as illustrated by the negative slope of the latter half of the curves. The experiments indicate that the maximum rate is obtained with mixtures of approximately constant composition irrespective of total pressure. In these optimum mixtures the rate is very nearly proportional to the square of acetylene concentration, as is shown by Table IV, while at relatively low oxygen concentrations the rate is proportional to the first or even lower power of acetylene.

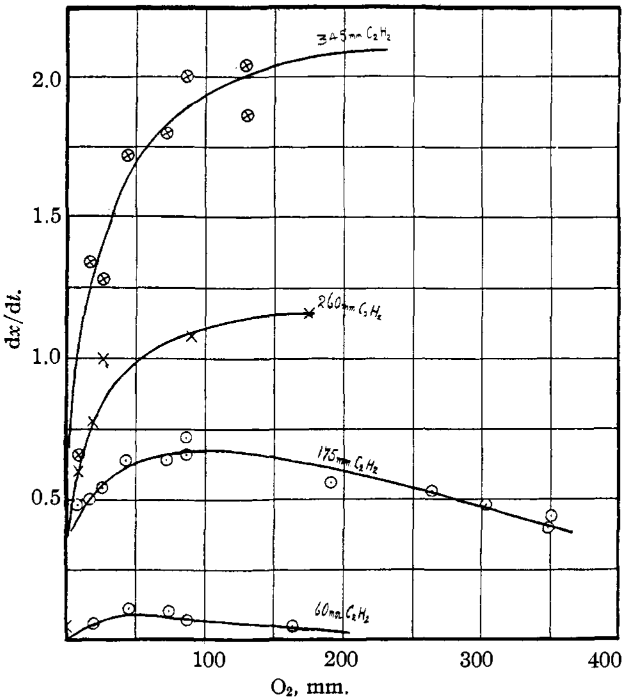

Fig. 4.—Oxygen concentration (for fixed acetylene concentration) plotted against rate of reaction (dx/dt); temp., 320°.

Table IV

Dependence on Acetylene

C_2H_2, mm.	O_2, mm.	C_2H_2/O_2	Max. dx/dt	$C_2H_2^2$/dx/dt
60.0	45.0	1.33	0.09	4.0
175.0	110.0	1.60	0.68	4.4
260.0	180.0	1.44	1.16	5.9
345.0	>230.0	<1.50	>2.10	<5.9

Influence of Nitrogen.—To investigate a possible effect of inert gases an experiment was performed with a large amount of nitrogen present. As appears from Table V, nitrogen has a slight retarding effect which is, however, even less pronounced than that of oxygen when the latter is present in excess.

TABLE V

INFLUENCE ON INERT GASES

No.	N_2, mm.	C_2H_2, mm.	O_2, mm.	Δp						dx/dt
				5 min.	10	15	20	25	30	
30		173.2	70.3	3.3	6.5	9.7	12.7	16.0	19.3	0.64
31	275.0	175.4	68.6	3.0	5.6	8.4	11.2	13.7	16.2	.56
44		173.3	348.1	...	3.9	...	7.8	..	11.5	.40

Products of the Reaction.—Table VI gives typical results of an analysis of the reaction products. Several sets of such determinations have been carried out on different reacting mixtures but, owing probably to uncertainties of the analysis, no systematic variations in the composition of the products could be detected.

TABLE VI

ANALYSIS OF REACTION PRODUCTS AND CARBON BALANCE

Expt. No. 36; C_2H_2, 357.0 mm.; O_2, 129.0 mm.; dx/dt, 2.04; time, 1 hour

Product	Amount	G. atoms $C \times 10^3$	Gm. atoms $C \times 10^3$ at beginning
$C_2H_2O_2$	0.0227 g.	0.783	
HCHO	.0163 g.	.545	
HCOOH	.0173 g.	.376	
C_2H_2	75.03%	19.180	23.960
CO_2	1.43	0.182	
O_2	7.71		
H_2	.....		
CO	21.90	2.798	
Totals		23.864	23.960

The iodine test gave no indication of the presence of a per-acid in the condensate.

Discussion of Results

The experiments here presented show that oxidation of acetylene can proceed at a perfectly reproducible rate and has well-defined kinetics. The reaction would, therefore, seem to lend itself readily to kinetic treatment. However, any theory of the reaction mechanism would have to account not only for the dependence of the rate—as measured by the manometer—on the concentrations of the reactants, but also for such things as the presence of an induction period and the fate of the intermediate products. It is in the attempt to bring all these phenomena together in one theory that the chief difficulty is encountered.

It seems fairly certain that the induction period is an inherent part of the reaction and is not due to impurities. Thus, Kistiakowsky and Lenher, working with a different method and using considerably less purified gases than in the present work, observed that the lower the temperature at which the reaction proceeded, the longer was the induction period. Using contact times of fifty to two hundred seconds, they failed to notice an induction period at 313°—the highest temperature then studied. This present research, however, shows that an induction period is present even at 320° but is of much shorter duration. The two sets of experiments agree well together and indicate that the length of the induction period is roughly, at least, inversely proportional to the rate of reaction. These facts, together with the character of the present experimental method—a continuous circulation of the gases with removal of condensible products—make it most probable that the induction period is caused by a gradual accumulation of some condensible substance which is necessary for the oxidation of acetylene to acquire its full rate. Since the induction period is of considerable duration, this catalytic substance must possess some degree of stability at the temperatures employed and it thus becomes very probable that it can be identified as one or all of the three condensible intermediate products described above: glyoxal, formaldehyde or formic acid. Although a definite proof of this conclusion is still lacking, some evidence can be brought forward to show that formaldehyde at least must take an active part in the acetylene reaction. According to the theory of Bone[3] formaldehyde is not a by-product but one of the main stages in the oxidation of acetylene, which seems most plausible to the present writers. Furthermore, the experiments of Askey[7] show that mixtures of pure formaldehyde and oxygen are quite stable at 320°, the time of half reaction being of the order of one hour. Thus with a contact time of less than a minute, one should expect to find all the reacted acetylene in the form of formaldehyde. Instead, it is found that the major part of the formaldehyde is oxidized further into formic acid, carbon monoxide and water, its stationary concentration in the reacting mixture being attained in less than a minute at 310° according to experiments of Kistiakowsky and Lenher.[1] This means that in presence of acetylene, formaldehyde is oxidized some hundred times faster than when alone. Owing to lack of experimental data, no similar comparison can be made in the case of glyoxal and formic acid.

The induction period and the behavior of formaldehyde lend additional evidence in favor of a chain mechanism of acetylene oxidation. There is a large series of possible mechanisms for this reaction. The simplest, which does not involve any unidentified intermediate products

$$\begin{aligned} C_2H_2 + O_2 &\longrightarrow C_2H_2O_2 \\ C_2H_2O_2 &\longrightarrow CO + HCHO \\ HCHO + O_2 &\longrightarrow CO_2 + H_2O \end{aligned}$$

must, however, be neglected, since it accounts neither for the observed dependence of the rate on the reactant concentration, nor for the induction period, the oxidation of formaldehdye, nor the presence of chains. Several other schemes involving the least possible number of intermediate reactants were tried and it was found that mechanisms involving, in addition to the substances actually isolated, a compound of the per-acid or per-

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[7] Askey, THIS JOURNAL, **52,** 974 (1930).

oxide type such as have been identified in many other oxidations, led to kinetic equations which could be made to reproduce the general trend of the experimental results. Schemes involving oxygen atoms were, in general, unsatisfactory. The equations derived from the per-acid theory, however, necessitated the assumption of chains sufficiently long that the primary reaction between acetylene and oxygen became insignificant in the total balance of reaction—in agreement with the observed retarding effect of the walls. On the other hand, assuming that each molecule of formaldehyde or glyoxal causes the oxidation of only one or two acetylene molecules, it can be calculated—from the amounts of the intermediary products recovered in the trap—that the chain length, *i. e.*, the number of acetylene molecules oxidized as the result of one primary reaction, does not exceed three to six. To reconcile these conclusions is difficult and it seemed to the writers that, until more experimental data are accumulated, an attempt to set up a detailed theory of the reaction mechanism would be premature. The constant K_0 of Table III was calculated therefore with the aid of an empirical equation

$$\frac{dx}{dt} = K_0 \frac{[C_2H_2]^2[O_2] + 3.5\,[C_2H_2]^2}{0.9\,[O_2] + 0.25\,\frac{[O_2]^2}{[C_2H_2]} + 0.0029\,\frac{[C_2H_2]^2}{[O_2]}}$$

which represents the observations reasonably well.

One of the authors (R. S.) wishes to express his indebtedness to the Commonwealth Fund for a Fellowship which enabled him to take part in this research.

Summary

1. The slow oxidation of acetylene has been studied by a circulation method allowing the isolation of more stable intermediate compounds.
2. It is found that these latter consist of glyoxal, formaldehyde and formic acid.
3. The rate of reaction is accelerated by oxygen when acetylene is in excess but is slightly retarded by it when present in excess.
4. 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.
5. Nitrogen has a very slight retarding influence on the rate.
6. The reaction exhibits an induction period which is due to gradual accumulation of an intermediary product taking part in the chain.
7. It is pointed out that in the presence of reacting acetylene, formaldehyde reacts with oxygen many times faster than when alone.
8. The bearing of these observations on the reaction mechanism is discussed.

PRINCETON, NEW JERSEY