

The Kinetics of the Oxidation of Gaseous Hydrocarbons III. The Oxidation of Acetylene

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factor; this probably arises from optical isomerism in many cases and from a variable association in the case of simple alcohols.⁸ In polyisobutylene, the steric hindrance of the long, clumsy chain molecules, and the variety of molecular species present, undoubtedly account for the failure to crystallize under any circumstances.

The temperature at which the transitions in heat capacity and thermal expansion occur seems in general to be connected with a viscosity of 10^{13} poises, and hence with a certain definite degree of intermolecular interaction. When glass-forming substances are arranged in the order of the mean temperatures of their transition regions, the series progresses regularly from nonpolar compounds through compounds of increasing dipole moment to a substance like boron trioxide, whose structure involves a network of valence bonds throughout. For equal dipole moments, the compounds fall in the order of increasing

molecular weights. Polyisobutylene, although virtually nonpolar, has a mean temperature of transition corresponding to rather polar compounds, falling between glycerol and lactic acid. This may be qualitatively explained on the basis of its huge molecular weight, which may be considered to overbalance the effect of the nature of the intermolecular forces. More specifically, we may consider the binding among the isobutylene units in the material. Binding between units in different macromolecules is of a purely van der Waals character, similar to the intermolecular interaction in nonpolar compounds. Units in the same macromolecule, however, are connected by chemical bonds—a type of binding more analogous to that in boron trioxide than to that in any other organic glass-forming material. The resultant of these two types of binding places the transition temperature of polyisobutylene somewhere between those of nonpolar heptanes (about 88°K) and boron trioxide (about 510°K).

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The Kinetics of the Oxidation of Gaseous Hydrocarbons

III. The Oxidation of Acetylene

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An investigation of the kinetics of the oxidation of gaseous acetylene has been made by the static method. The results show marked irregularities due to variations in the surface. The rate of the reaction is given by

$$-(d/dt)(C_2H_2) = K(C_2H_2)^{2.7}/(O_2)^{0.1}$$

when oxygen is in excess. In a packed bulb the order is diminished to about 1.4. Packing decreases the rate at high pressures and has little effect at low pressures. In an empty

vessel the CO/CO₂ ratio of the products is independent of the pressure. Packing decreases this ratio, and it further decreases rapidly with diminishing pressure. The apparent heat of activation of the reaction is about 35,000 calories. The addition of glyoxal to the reaction mixture causes no change in the rate of the reaction, while formaldehyde causes a marked retardation. The products of the reaction are discussed in the light of recent work on the oxidation and decomposition of glyoxal.

INTRODUCTION

THERE have been a number of previous investigations of the oxidation of acetylene. Bone and Andrew¹ interpreted their work by postulating the formation of the unstable dihydroxy compound C₂(OH)₂, which was assumed

to decompose directly into CO and HCHO. In a more recent investigation, Kistiakowsky and Lenher² found that the reaction was a chain process with the rate proportional to the square of the acetylene concentration, and a slight retardation by oxygen. The condensable products

¹ Bone and Andrew, J. Chem. Soc. **87**, 1232 (1905).

² Kistiakowsky and Lenher, J. Am. Chem. Soc. **52**, 3785 (1930).

were mainly glyoxal, formaldehyde, and formic acid. They suggested that the primary step in the reaction was the formation of glyoxal, which subsequently was oxidized or decomposed. They did not attempt to arrive at the chain process. The investigation was further extended by Spence and Kistiakowsky.³ After a further investigation, Spence⁴ proposed a mechanism for the reaction based in principle on the Bodenstein scheme, activated glyoxal being assumed to carry the chains.

The present paper deals with an investigation of the acetylene oxidation by the static method, with special emphasis on high oxygen concentrations and on the effect of surface. Experiments have also been made on the oxidation of mixtures of acetylene and glyoxal, and of acetylene and formaldehyde to determine the possibility of these substances acting as carriers of the reaction chains.

EXPERIMENTAL

The change in pressure accompanying the oxidation of acetylene is too small to permit its use as a method of following the reaction, and it was therefore decided to investigate the reaction by withdrawing samples of gas for analysis from time to time. The apparatus was similar to that employed in previous investigations.⁵ Mixtures of oxygen and acetylene were made up and introduced into silica or Pyrex reaction vessels of about 200 cc capacity at the desired temperature. After a definite time the gaseous mixture was withdrawn and analyzed in a Burrell gas analysis apparatus.

The oxygen used was taken directly from cylinders of the commercial gas and dried over phosphorus pentoxide. Analysis showed it to contain from 1.0 to 1.4 percent nitrogen. Acetylene was generated from calcium carbide, and was washed with solutions of potassium hydroxide, chromic acid, mercuric chloride in hydrochloric acid, and alkaline hydrosulphite. It was then dried and condensed with liquid air and fractionated. From 98.7 to 99.4 percent was absorbed in fuming sulphuric acid.

In theory the use of the analytical method is extremely simple. A number of experiments are performed under identical conditions, and are interrupted and a sample taken at various times. We may then construct a rate curve and from it determine either the velocity constant or the time to half-value. The great disadvantage of the method is that each experiment gives only a single point on the amount reacted-time curve, and the investigation is thus exceedingly laborious.

The method used here to avoid this is as follows. The value of, say, T_{50} is obtained under one set of conditions from a series of experiments as described above. Then to determine the order another experiment is performed at a higher pressure and the sample is withdrawn at a time which would correspond to 50 percent reaction if the reaction had some plausible assumed order, say 2. Since the order is not exactly 2, the amount reacted as determined by analysis is not 50 percent, but say 55 percent. The order is thus more than 2, and since the percent reacted is not very different from 50, the time for 50 percent reaction can be calculated to a fair approximation still assuming an order of 2. An approximate graph of T_{50} against pressure is obtained in this way, and hence the approximate order. The calculations are then repeated with this more accurate value of the order, and the real order is thus found by successive approximations from only one experiment at each pressure.

The amount of reaction has in every case been inferred from the percentage of unchanged acetylene in the gaseous reaction products. The calculation can only be made, however, provided that no condensable products are present, or that the amount and composition of such products is known. As will be shown later, on the average about 5 percent of the total carbon goes to form such condensable products, and all calculations of the amount of reaction have been made on this assumption.

EXPERIMENTAL RESULTS

The pressure change accompanying the reaction

As mentioned at the outset, the pressure change accompanying the reaction is comparatively small. The actual pressure increase found

³ Spence and Kistiakowsky, *J. Am. Chem. Soc.* **52**, 4837 (1930).

⁴ Spence, *J. Chem. Soc.* **1932**, 686.

⁵ Steacie and McDonald, *J. Phys. Chem.* **38**, 1031 (1934).

varied widely with the experimental conditions. The pressure-time curves, however, always had roughly the same form, the pressure decreasing very slightly at the start and then rising. Almost without exception, it was found that, for corresponding stages of the reaction, the relative pressure changes were greater the lower the initial pressure. Depending upon the conditions, the pressure increase corresponding to 50 percent reaction varied from 3 to 11 percent. With a packed reaction vessel the form of the pressure time curves was completely altered, and the pressure decreased steadily but very slightly.

The order and the rate of the reaction

The rate of the reaction was found to be very variable, and to be strongly dependent upon the condition of the surface of the reaction vessel. On this account a number of different vessels were used which had been subjected to various surface treatments. The different series of experiments are described below.

Series I. A mixture consisting of $2\text{O}_2 + 1\text{C}_2\text{H}_2$ was used at 320°C . The reaction vessel was a spherical Pyrex bulb. It was washed and given a prolonged evacuation at 550°C . The rate was found to increase steadily for some 40 runs. Heating to 550°C with and without air between runs had no effect on the results. Little information could be obtained from this series, except that the over-all order of the reaction was between 2 and 3.

Series II. The reaction vessel was a Pyrex bulb as before. It was rinsed with a normal solution of NaCl, and then once with distilled water, a treatment which Lenher and Kistiakowsky found to speed up the reaction and to make the results more reproducible. In the present work the rate was increased, but the drift was very pronounced and after a few runs the bulb was discarded.

Series III. A spherical Pyrex vessel of 200 cc capacity was used. It was rinsed with a saturated solution of potassium chloride and evacuated. The aging in this case was much less pronounced, but was still somewhat troublesome. The results will therefore not be given in detail. Runs were made with 2:1, 3:1, and 5:1 mixtures. These indicated an order between 2.4 and 2.6, and

that oxygen had a very slight retarding effect on the reaction.

Series IV. The same vessel as in III was used after a further treatment with saturated potassium chloride solution. The reproducibility in this case was excellent and about 25 runs were made. The gas analyses are given in detail in Table I. It will be seen from the constancy of the $(\text{CO} + \text{CO}_2)/\text{C}_2\text{H}_2$ ratio, which is obviously a measure of the amount of reaction, that the times chosen for sampling correspond almost exactly to equal amounts of reaction. The corrections which must be made, as described above, are very little greater than the experimental error. These corrections have been made, and the results are given in Fig. 1 in the form of a $\log T_{45} - \log P_{\text{C}_2\text{H}_2}$ graph.

As shown by Table I, the CO/CO_2 ratio of the products remains constant for any $\text{O}_2/\text{C}_2\text{H}_2$ ratio. It also varies very little with the different mixtures. Thus on going from a 1:1 to a 5:1 $\text{O}_2/\text{C}_2\text{H}_2$ mixture the CO/CO_2 ratio falls only about 10 percent.

From the slopes of the lines in Fig. 1, the over-

TABLE I. Gas analyses from series IV.

TEMPERATURE = 320°C $P_{\text{C}_2\text{H}_2}$			A = CO/CO ₂					B = (CO + CO ₂)/C ₂ H ₂		
No.	Initial (cm)	t (min.)	Composition of sample—%						A	B
			CO ₂	C ₂ H ₂	O ₂	CO	H ₂	N ₂		
ORIGINAL MIXTURE—O ₂ /C ₂ H ₂ = 1										
18	21.5	9.8	8.8	31.6	20.2	37.4	2.0		4.25	1.46
20	19.6	11.6	8.3	32.1	20.0	37.4	2.2		4.50	1.42
21	15.7	17.8	8.2	31.4	21.3	37.2	1.9		4.54	1.44
22	12.5	27.6	8.0	31.5	21.6	37.0	1.9		4.63	1.43
19	10.8	36.4	8.1	31.6	20.6	37.5	2.2		4.63	1.44
ORIGINAL MIXTURE—O ₂ /C ₂ H ₂ = 2										
1	20.5	10.6	6.1	20.3	48.0	23.9	1.7		3.92	1.48
2	16.5	16.0	6.0	20.2	47.6	24.2	2.0		4.03	1.49
13	14.6	19.6	5.6	20.1	48.0	24.3	2.0		4.34	1.49
3	13.2	23.6	5.8	20.3	47.8	24.3	1.8		4.20	1.48
4	10.5	34.6	5.6	20.5	48.4	23.7	1.8		4.24	1.43
5	8.4	51.8	5.4	20.5	48.2	24.1	1.8		4.27	1.44
ORIGINAL MIXTURE—O ₂ /C ₂ H ₂ /N ₂ = 2/1/1										
6	15.2	18.2	4.1	14.6	34.6	17.5	0.7	28.5	4.26	1.48
7	12.2	26.6	4.0	14.7	34.3	17.6	0.6	28.8	4.40	1.47
ORIGINAL MIXTURE—O ₂ /C ₂ H ₂ = 3										
16	15.8	17.5	4.3	14.5	62.0	17.4	1.8		4.05	1.50
17	12.7	25.6	4.1	14.8	62.6	16.8	1.7		4.10	1.41
14	10.0	38.8	4.2	14.8	61.5	17.7	1.8		4.22	1.48
15	7.9	57.2	4.2	14.6	62.0	17.4	1.8		4.14	1.48
ORIGINAL MIXTURE—O ₂ /C ₂ H ₂ = 5										
8	10.3	38.0	3.1	9.6	74.0	11.6	1.7		3.74	1.53
9	8.2	56.5	2.9	9.7	74.0	11.7	1.7		4.03	1.51
10	6.5	83.0	2.9	9.5	74.4	11.4	1.8		3.93	1.51
ORIGINAL MIXTURE—O ₂ /C ₂ H ₂ /N ₂ = 5/1/1										
11	9.0	48.0	2.4	8.1	63.4	9.6	0.0	16.5	4.00	1.48
12	7.1	71.5	2.5	8.1	63.2	9.4	0.0	16.8	3.76	1.48

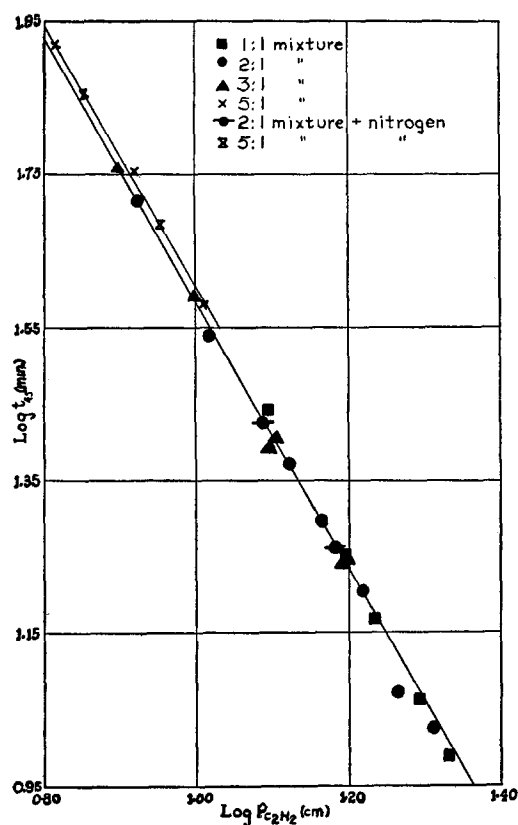


FIG. 1. The effect of pressure on the rate of reaction.

all order is calculated to be 2.7. The 5:1 mixture indicates a slight retardation by oxygen. In the other cases any effect of the oxygen concentration is smaller than the experimental error.

In the runs in which nitrogen was added it is possible to set up material balances and to calculate the amount of condensable products formed. A few typical results of this kind are given in Table II. It will be noted that approximately 5 percent of the total carbon present appears as condensable material. The amount of condensable products present is too small to permit of an accurate calculation of its composition.

Series V. After the completion of the above

TABLE II. Material balances—series IV.

RUN No.	7			11			12		
	C	H	O	C	H	O	C	H	O
Calculated	53.6	53.6	107.0	29.1	29.1	143.0	29.6	29.6	145.4
Found	51.0	30.6	94.2	28.2	16.2	141.2	28.1	16.2	140.8
Difference	2.6	23.0	12.8	0.9	12.9	1.8	1.5	13.4	4.6

experiments in Series IV, aging effects again became apparent. A spherical 200-cc silica bulb was therefore tried. After a few experiments in which the rate increased progressively from run to run, conditions became steady and some 50 runs showed excellent reproducibility. These confirmed almost exactly the conclusions reached with the Pyrex bulb, showing an over-all order of about 2.6 and again a slight retardation due to oxygen. The absolute rates in the silica bulb were, however, about 30 percent higher than those in the Pyrex bulb. Material balances and the analyses of the products were also in excellent agreement with Series IV. The material balances, however, showed much better agreement among themselves and thus permitted a rough estimate of the composition of the condensable material. Some typical results are summarized in Table III.

In view of the difference between the value of the order of the reaction found here and that found by Spence and Kistiakowsky, it was of importance to determine whether the order varied with the stage of the reaction as has often been reported for hydrocarbon oxidations. A number of experiments were therefore made at different pressures with a $3\text{O}_2 : 2\text{C}_2\text{H}_2$ mixture. Samples were withdrawn and analyzed at times corresponding approximately to T_{25} and T_{70} instead of to T_{45} as before. These indicated an order identical with the previously found value. The ratios $T_{25} : T_{45} : T_{70}$ were also in agreement with the calculated ratios for an order of 2.6. Hence it may be concluded that the over-all order of the reaction is 2.6 over at least 75 percent of its course.

The temperature coefficient

A separate series of experiments was made in a silica vessel to determine the temperature coefficient.

TABLE III. Composition of condensable products in typical experiments.

% C	% COMPOSITION OF CONDENSABLE MATERIAL		% OF TOTAL CARBON IN THE CONDENSABLE PRODUCTS
	H	O	
10.0	61.1	28.9	7.6
9.0	63.0	28.0	6.7
9.4	61.8	28.8	7.2
9.2	57.0	33.8	7.5
8.8	59.2	32.0	7.0
7.8	59.2	33.0	6.5
8.3	65.5	26.2	5.8
9.9	63.8	26.3	5.5

TABLE IV. *The temperature coefficient of the reaction.*

PRESSURE—13.0 CM		2O ₂ : 1C ₂ H ₂ MIXTURE							
TIME (min.)	TEMP. (°C)	COMPOSITION OF			SAMPLE—%		CO	CO	T ₄₅
		CO ₂	C ₂ H ₂	O ₂	CO	Res.	CO ₂	CO+CO ₂ C ₂ H ₂	(calc.)
140	280	6.5	18.8	47.3	24.6	2.8	3.79	1.65	118
46.3	300	6.8	17.9	44.5	28.1	2.7	4.13	1.95	32.0
16.5	320	6.3	17.9	45.7	27.5	2.3	4.36	1.89	11.7
6.6	340	5.7	18.9	46.8	26.0	2.6	4.55	1.68	5.4

cient of the reaction. The results are given in Table IV. From the values of T_{45} the activation energy is calculated to be 33,500 calories, in good agreement with the value of 34,700 calories found by Spence and Kistiakowsky. The values of T_{45} in Table IV have been calculated on the assumption that the order does not change with changing temperature. While this may not be strictly true, the correction involved is comparatively small and the value of E would not be very much affected by a small change in order. In any case, in the absence of any very definite significance for the temperature coefficient, it was not considered worth while making an exhaustive investigation to establish it more accurately.

The effect of surface

The effect of increased surface was investigated with a cylindrical silica bulb of about 125 cc capacity. The packing consisted of short lengths of thin silica capillary tubing, and was rather loose, the top quarter of the bulb being empty. The results are given in Table V.

It is apparent that with increased surface:

- The rate is decreased at high pressures. At low pressures there is an apparent small increase in rate.
- The order of the reaction in the packed bulb is much lower than usual, being only about 1.4.
- There is a very marked decrease in the CO/CO₂ ratio in the packed bulb. In the unpacked bulb the CO/CO₂

TABLE V. *The effect of increased surface.*

TEMPERATURE 320°C			2O ₂ : 1C ₂ H ₂ MIXTURE		
P _{C₂H₂} (cm)	T ₂₅ (min.)	CO/CO ₂ (products)	P _{C₂H₂} (cm)	T ₂₅ (min.)	CO/CO ₂ (products)
<i>Packed bulb</i>			<i>Unpacked bulb</i>		
22.8	25.0	1.56	22.5	16.0	2.52
19.9	27.3	1.21	19.8	18.2	2.32
17.4	30.8	1.08	17.0	25.9	2.37
12.7	34.8	0.71	14.6	29.2	2.48
12.3	34.0	0.65	12.5	34.0	2.49
10.1	36.1	0.58	11.3	38.8	2.57
9.4	36.8	0.47			

TABLE VI. *The effect of added glyoxal and formaldehyde.*

TEMPERATURE 320°C		2O ₂ : 1C ₂ H ₂ MIXTURE		
P _{C₂H₂} (cm)	TIME (min.)	ADDED GAS	PARTIAL PRESSURE OF ADDED GAS (cm)	% OF ACETYLENE REACTED
12.4	17.7	none	—	23.0
12.4	17.7	glyoxal	1.1	23.6
9.6	26.5	none	—	22.6
9.6	26.5	glyoxal	2.6	25.8
12.3	27.0	none	—	24.3
12.3	27.0	formaldehyde	1.1	17.3
9.0	44.3	none	—	28.2
9.0	44.3	formaldehyde	5.3	9.8

ratio is independent of the pressure. In the packed bulb, however, the ratio decreases rapidly with decreasing pressure.

These points will be discussed later.

The effect of additions of glyoxal and formaldehyde

Since glyoxal has often been assumed to play an important part in the oxidation of acetylene, it was of interest to determine the effect of its addition upon the rate of the reaction. A number of experiments were therefore made with and without added glyoxal, and the results are given in Table VI. In each case a known amount of nitrogen was present, so that the amount of acetylene which had reacted could be calculated from analyses of the gaseous products. It will be seen from Table VI that glyoxal has no influence on the rate when it is present in small quantities. At high glyoxal concentrations there is a very slight acceleration of the reaction, but this is probably merely due to the heat developed in the very rapid glyoxal oxidation causing a temporary interruption of isothermal conditions.

The data for similar experiments with formaldehyde are also given in Table VI. It will be seen that formaldehyde has a definite retarding action, which becomes very pronounced at high formaldehyde concentrations. It should be pointed out that an interval of about two weeks occurred between the experiments with glyoxal and those with formaldehyde. During this time considerable aging had occurred, and hence the times for the first 4 experiments in Table VI cannot be compared with those for the last 4 experiments.

DISCUSSION

As we have seen, the over-all order of the reaction is 2.6, with a slight retardation by oxygen. The results can therefore be approximately expressed by

$$-(d/dt)(C_2H_2) = K(C_2H_2)^{2.7}/(O_2)^{0.1},$$

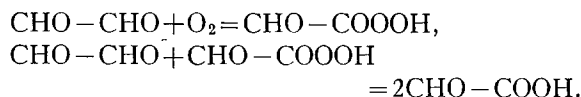
provided that oxygen is in excess. This is rather higher than the order of about 2 found in previous investigations. However, the order diminishes strongly in a packed bulb, and hence in the narrower vessels used in previous investigations by the flow method we would expect the order to be somewhat diminished.

Previous work has indicated the presence of an induction period. The form of the pressure-time curves obtained here (an initial small pressure decrease followed by an increase) suggests that the induction period is to be attributed to the building up of a stationary concentration of some intermediate substance. Curves of this form would be difficult to interpret merely on the conception of an initial time required for the development of branching chains.⁶

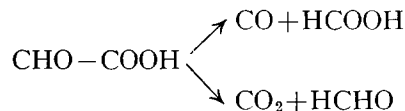
The main point is to account in a reasonable manner for the products of the reaction and their variation with changing surface-volume ratio. There seems to be no doubt that glyoxal is one of the most important products of the reaction, and in previous discussions of the mechanism of the reaction the fate of glyoxal has always played a prominent part. In view of the recent investigations of the oxidation and decomposition of glyoxal made in this laboratory,⁷ it now seems possible to account for the products of the reaction without being obliged to assume that the intermediate substances react in a way which is contrary to their normal behavior.

We may assume, as has been done almost invariably in the past, that glyoxal is the first recognizable product of the acetylene oxidation. It has recently been shown that at the temperatures used here the glyoxal decomposition is negligibly slow and leads in part to the formation of tarry materials. It may therefore be concluded that none of the glyoxal formed disappears by

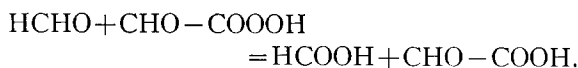
decomposition. The oxidation of glyoxal is exceedingly rapid at 320°C, and we may assume that it follows its usual course, *viz.*,



At about 200°C a considerable amount of CO and CO₂ are formed in the glyoxal oxidation, but a large amount of glyoxylic acid survives. At the higher temperatures used here it is not surprising that glyoxylic acid is not detected as a product, especially since the usual tests do not distinguish between trimeric glyoxal and glyoxylic acid. The main fate of the glyoxylic acid will be



It may be remarked that under normal conditions glyoxylic acid does not oxidize to oxalic acid, although it is, of course, possible that some glyoxylic acid disappears by complete oxidation to the oxides of carbon and water. In the glyoxal oxidation the CO/CO₂ ratio of the products is about 3, and hence we may assume that the decomposition of glyoxylic acid to CO and HCOOH predominates. Formic acid can then disappear by decomposition in the usual way. At the temperatures used here, however, the decomposition and oxidation of formaldehyde are quite slow, and Spence has pointed out that in the acetylene oxidation formaldehyde must be oxidized at about 100 times its normal rate. It has recently been shown that various aldehydes oxidize by identical mechanisms,⁸ and it therefore seems reasonable to assume that formaldehyde is oxidized by replacing glyoxal in the reaction with glyoxylic peracid, *viz.*,

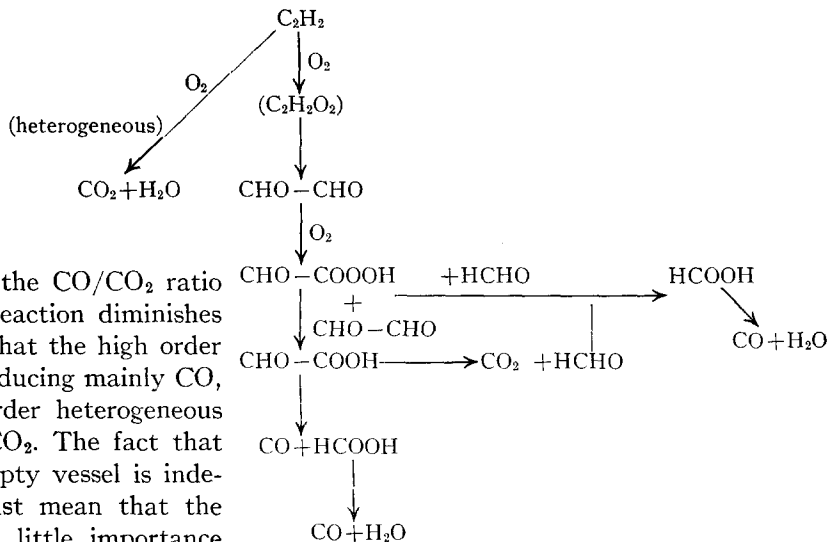


Hence as a complete scheme for the course of the reaction we have

⁶ See Kontorovna and Neumann, *Physik. Zeits. Sowjetunion* **4**, 818 (1933).

⁷ Hatcher, Horwood and Steacie, *J. Chem. Phys.* **3**, 291, 551 (1935).

⁸ Hatcher, Steacie and Howland, *Can. J. Research* **5**, 648 (1931); **7**, 149 (1932). Steacie, Hatcher and Rosenberg, *J. Phys. Chem.* **38**, 1189 (1934). Hatcher, Horwood and Steacie, reference 7.



The effect of surface

On increasing the surface the CO/CO₂ ratio falls, and the order of the reaction diminishes to about 1.4. This suggests that the high order chain reaction in the gas, producing mainly CO, is accompanied by a low order heterogeneous reaction producing mainly CO₂. The fact that the CO/CO₂ ratio in the empty vessel is independent of the pressure must mean that the heterogeneous reaction is of little importance when the surface is small. On increasing the surface, however, the heterogeneous reaction is favored by a factor of about 6, while the homogeneous reaction is retarded by the chain-breaking effect of the surface, and hence in the packed bulb the surface reaction becomes prominent. Since the surface reaction has a low order, its influence will be greatest at low pressures, and hence in the packed bulb the CO/CO₂ ratio diminishes with decreasing pressure. The retarding effect of the increased surface also falls off at low pressures, since the increase in the heterogeneous process makes up for the decrease in the homogeneous reaction.

To the foregoing scheme for the course of the reaction, therefore, we must add a heterogeneous oxidation of acetylene to CO₂, which is not of much importance unless the surface-volume ratio is high.

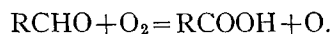
The chain mechanism

The very great sensitivity of the rate of reaction to changes in the condition of the surface makes it apparent that the surface is important either for the initiation or for the breaking of reaction chains. The retarding effect of increased surface, however, is not great, and inert gases have little or no accelerating effect on the reaction. It seems certain, therefore, that the wall is of paramount importance in the initiation of the chains, and does not participate in their destruction to a very great extent.

As in most organic oxidation reactions, it is

not possible to infer the carriers of the chains with any degree of certainty. The experiments with added glyoxal and formaldehyde show, however, that normal glyoxal and formaldehyde and their products of oxidation are not the chain carriers. We may therefore exclude glyoxal, glyoxylic acid, glyoxylic peracid, formaldehyde, and formic acid. We may of course assume that in an energy chain one of these products will act as a carrier when it is in an activated state. Since presumably such a substance must be activated before it oxidizes, this necessitates the assumption of different activated states for the same molecule in different, but equally exothermic, reactions. This does not appear very plausible, and it seems more reasonable to assume that the chain carrier is some product which precedes glyoxal. From this point of view a mechanism of the Bodenstein type appears the least objectionable.

Norrish has recently suggested⁹ a general theory of hydrocarbon oxidation involving a free radical-oxygen atom chain. On the basis of this mechanism the initiation of the chains occurs by the reaction



The pertinent aldehydes in this case are glyoxal and formaldehyde, and since both have been shown to have no sensitizing effect on the reaction, it appears unlikely that such a mechanism can hold for the oxidation of acetylene.

⁹ Norrish, Proc. Roy. Soc. A150, 36 (1935).