7. The absorption rates of several olefin gases by sulfuric acid both at rest and stirred beneath its surface have been measured. The values for the absorption coefficients agree well with those obtained in a previous investigation using a rotating absorbing chamber.

8. The reactions between the olefins and sulfuric acid take place mainly in the liquid stationary film itself. This is indicated (a) by the enormous rates of absorption obtained in some cases, although the physical solubilities of the gases in the acid appear to be very low and (b) by the fact that stirring the acid underneath the surface or changing its volume, in most cases, did not change the absorption rate. The reaction rates of the dissolved olefins are quite fast and are not proportional to the absorption rates as is often assumed.

9. The fact that isobutene is absorbed by 60% sulfuric acid faster when the acid is at rest than when it is stirred is attributed to a greater accumulation of the reaction product, *tert.*-butyl alcohol, in the liquid stationary film of the quiescent acid.

10. It is suggested that the over-all rate of absorption of ethylene by concentrated sulfuric acid (the rate per unit area being independent of the agitation) may be used to determine the area of the surface of a liquid when stirred or shaken in an apparatus.

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STUDIES IN GASEOUS OXIDATIONS. I. THE HOMOGENEOUS UNCATALYZED REACTION BETWEEN OXYGEN AND ACETYLENE

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The problem of the oxidation of hydrocarbons has been of great scientific and technical interest for many years. The present work was undertaken to study in detail the features of a simple hydrocarbon oxidation in the hope that it would contribute to the general knowledge of the mechanism of gaseous oxidations. Acetylene was chosen because it reacts with oxygen at lower temperatures than other hydrocarbons; this made it possible to isolate intermediate reaction products.

A systematic study of the slow reaction of simple hydrocarbons was initiated by Bone[1] about thirty years ago. More recently Pease[2] and also

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[1] Bone and Townend, "Flame and Combustion in Gases," Longmans, Green and Co., London, 1927.

[2] Pease and Chesbro, *Proc. Nat. Acad. Sci.*, 14, 472 (1928).

Pope, Dykstra and Edgar[3] and Thompson and Hinshelwood[4] have described experiments dealing with the slow thermal oxidations of the hydrocarbons by oxygen. Pease in particular has demonstrated that these reactions can occur in the gas phase exclusively and are inhibited by glass surfaces,[5] a characteristic of chain reactions.

Bone and Andrew[6] studied the combustion of acetylene in sealed bulbs between 200 and 350°. They concluded that an excess of oxygen over and above an equimolecular proportion always retards the oxidation, and postulated the presence of an unstable product $C_2H_2O_2$(HOC≡COH), which decomposed directly to carbon monoxide and formaldehyde. Recently Briner and Wunenburger,[7] in studying the reaction between acetylene and ozone at low temperatures, found the liquid products of reaction to be mainly glyoxal, CHO—CHO.

Experimental Results

The oxidation of acetylene was studied by the flow method at atmospheric pressure. Acetylene and oxygen at a regulated rate of flow passed through separate purifying trains and were mixed at the entering point of the reaction vessel. Both gases were taken from commercial cylinders. Oxygen was freed from water vapor by passing it through two wash-bottles filled with concentrated sulfuric acid. Acetylene (Prest-O-Lite) was passed through two spiral wash-bottles containing water to remove acetone vapor and was dried over calcium chloride. The pyrex cylindrical reaction vessel, 22 mm. in diameter, was heated in a large electric tube-furnace. Temperatures were read by means of a chromel–alumel thermocouple enclosed in a thin-walled glass tube placed in the center of the reaction vessel.

The gases, after passing through a trap cooled in solid carbon dioxide, were led through a spiral wash-bottle containing a standardized barium hydroxide solution to absorb carbon dioxide quantitatively, and were collected in a water gasometer. The gas was transferred to a 500-cc. Hempel pipet containing alkaline pyrogallol solution and shaken until all oxygen was consumed; it was then transferred to a bromine water pipet, and acetylene was removed by shaking; bromine vapor was removed from the residual gas by shaking with potassium iodide solution in a small Hempel pipet. The gas was then analyzed for carbon monoxide and hydrogen in a Burrel gas analysis apparatus[8] after checking for absence of oxygen and acetylene. Gases originally containing less than 1% of carbon monoxide could be analyzed satisfactorily. Carbon dioxide was determined by titrating the barium hydroxide solution with hydrochloric acid. The condensable reaction products were determined by oxidation with standardized potassium dichromate solution in concentrated sulfuric acid and iodimetric titration of the excess potassium dichromate. The potassium dichromate solution was added from a buret to the trap while still cold so that even volatile products (formaldehyde) were included in the analysis. The condensable products were mainly formic acid and

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[3] Pope, Dykstra and Edgar, THIS JOURNAL, **51**, 2203, 2213 (1929).

[4] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **125A**, 277 (1929).

[5] Semenoff, *Z. Physik*, **46**, 109 (1927).

[6] Bone and Andrew, *J. Chem. Soc.*, **87**, 1232 (1905).

[7] Briner and Wunenburger, *Helv. Chim. Acta*, **12**, 786 (1929).

[8] Bureau of Mines Bulletin No. 197, 1926; Bureau of Mines Technical Paper, No. 320, 1925.

formaldehyde. Checks with standardized formic acid solution showed that two equivalents of iodine are consumed in the oxidation of formic acid by potassium dichromate, the reaction being

$$HCOOH + {}^{1}/_{2}O_2 = CO_2 + H_2O$$

Oxidation of formaldehyde requires very nearly four (3.6) equivalents of iodine, the principal reaction being

$$CH_2O + O_2 = CO_2 + H_2O$$

although the other reaction

$$CH_2O + {}^{1}/_{2}O_2 = CO + H_2O$$

takes place to some extent.

A standard gas mixture containing equal volumes of acetylene and oxygen was used. The rate of flow of each gas was 0.1 cc./second, corresponding to an average contact time of 200 seconds for a 78-cc. vessel at an average temperature of 290°. Three hundred and sixty cubic centimeters of acetylene–oxygen mixture was used. Table I presents the results of these experiments. The amounts of formic acid and formaldehyde given in the last column have been calculated on the assumption that no other condensable products were present, and that these two substances were present in the ratio 6:1. Justification for this assumption will be given below in the discussion of the condensable products. From Table I it will be seen that the main products of acetylene oxidation are carbon monoxide and the "condensable matter." Carbon dioxide is also formed in considerable quantities whereas hydrogen, although present, plays a much less important role.

TABLE I

EFFECT OF TEMPERATURE ON REACTION OF OXYGEN WITH ACETYLENE

Average time of contact, 200 seconds

	Moles passed × 10^3		Moles formed × 10^3			
Temp., °C.	C_2H_2	O_2	CO	CO_2	H_2	HCOOH + HCHO
253	8.9	8.9	0.109	0.069	0.009	0.07
255	8.9	8.9	.074	.005	.022	.14
256	8.9	8.9		.021		.18
256	8.9	8.9	.126	.032		.07
Av. 255	8.9	8.9	.105	.032	.015	.11
Percentage of total carbon passed			.49	.18		.63
277	8.9	8.9	.25	.090	.043	.23
277	8.9	8.9	.43	.096	.057	.25
277	8.9	8.9	.29	.069	.039	.30
277	8.9	8.9	.25	.080	.035	.29
Av. 277	8.9	8.9	.30	.084	.043	.26
Percentage of total carbon passed			1.71	.43		1.50
296	8.9	8.9	0.99	.33	.087	
296	8.9	8.9	1.30	.38	.130	0.99
297	8.9	8.9		.39		.91
298	8.9	8.9		.40		.67
Av. 297	8.9	8.9	1.14	.37	.108	.84
Percentage of total carbon passed			6.4	2.1		4.7
315	8.9	8.9	2.67	0.80	.18	1.59
315	8.9	8.9	2.86	.70	.26	1.10
316	8.9	8.9	2.90	.77	.26	1.62
318	8.9	8.9	3.17	.91	.33	1.70
Av. 316	8.9	8.9	2.90	.80	.26	1.50
Percentage of total carbon passed			16.3	4.5		8.4

The composition of the condensable products, which in the above experiments were measured only by the amount of potassium dichromate consumed, was determined with a sample obtained by carrying out the reaction for twelve hours at 310–315°. One and six-tenths grams of condensed products was collected in the cooled trap and diluted with two cc. of water.

The resulting solution was opaque, and a small quantity of a resinous substance collected at the surface on standing. Small samples were withdrawn from the solution and analyzed. The condensate gave a positive test for formic acid, using the mercuric oxide test.[9] Titration of two samples with barium hydroxide indicated 56.1 and 53.3% of formic acid. Oxalic acid was not present, for no precipitate of barium oxalate was formed. Formaldehyde was determined by two methods: the potassium cyanide reaction,[10] which yielded in three determinations 4.7, 4.7 (small samples) and 5.4% (large sample) by weight, and the iodimetric method,[10] which yielded in three determinations 9.2, 8.3 and 8.9% by weight. These determinations accounted for about 65% by weight of the condensate. The chemical nature of the remainder was established by titrating another sample with standard potassium dichromate solution. If it is assumed that formic acid and formaldehyde were present in the ratio 55:9, the oxidation analysis gave their total amount as 71.7% of the condensate. The remaining 28.3% was non-oxidizable and was undoubtedly water.

The discrepancy between 64% obtained by acid and aldehyde determinations and 72% calculated from oxidation analyses we suspected was fictitious, and was due to the assumption that formaldehyde was the only aldehyde present. Condensate was collected for thirty hours to obtain material to test this point. This was added to a solution of 5 g. of *p*-nitrophenylhydrazine in 50% acetic acid solution and allowed to stand for thirty-six hours. The brick red precipitate was filtered off, neutralized with warm 10% sodium carbonate solution, washed with hot distilled water and dried. The precipitate was extracted with hot benzene to dissolve the nitrophenylhydrazone of formaldehyde.[11] The residue was recrystallized from hot pyridine, yielding brick red needles melting over the range 250–270°. As the di-*p*-nitrophenylhydrazone of glyoxal is the only probable *p*-nitro or di-*p*-nitrophenylhydrazone having a higher melting point than that of the formaldehyde compound (185°), it seemed clear that we were dealing with the glyoxal derivative. The di-*p*-nitrophenylhydrazone of glyoxal was prepared from glyoxal sodium bisulfite compound and on recrystallization gave a melting point of 305°. When the pure di-*p*-nitrophenylhydrazone of glyoxal was mixed with the derivative from the condensate (m. p. 250–270°), the mixture did not melt at 278°, but decomposition took place. The di-*p*-nitrophenylhydrazone of glyoxal derived from the condensate gave the characteristic Bamberger test[12] of a deep blue color with alcoholic potassium hydroxide. The characteristic color of the derivative from the condensate, the high melting point as well as the mixed melting point, and finally the color test shows that glyoxal was present in appreciable quantities in the condensate.

To complete the analysis of the condensable products, the water-insoluble resinous substance (3.78 mg.) was subjected to microcombustion after it had been dried for twenty-four hours by exposure to the atmosphere. This yielded 52.71% carbon, 8.65% hydrogen and 1.77% ash, the rest being undoubtedly oxygen. Such a compo-

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[9] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1905**, Vol. I, p. 83.

[10] Allen, "Commercial Organic Analysis," 5th ed., P. Blakiston's Son Co., Philadelphia, **1927**, Vol. I, p. 329.

[11] Rosenthaler, "Der Nachweis organischer Verbindungen," Verlag Ferdinand Enke, Stuttgart, **1923**, 2d ed., p. 125.

[12] Bamberger, *Ber.*, **32**, 1806 (1899).

sition does not correspond to any single substance probable under the circumstances and it must be assumed that a mixture was present. If one attributes all of the oxygen to water present in the analyzed sample (41.5% by weight), the composition is 1.0 carbon:0.92 hydrogen, approximating the composition of acetylene. The behavior of the sample is further support for this assumption of water in the resinous matter, for it appeared to dry or harden on standing.

The effect of the time of contact on the speed of reaction and its course was studied by increasing the rate of flow. Results of these measurements made at two temperatures are presented in Tables II and III. In the experiments given in Table III, the condensate was weighed and the acid content determined by titration with barium hydroxide. The results of this determination are given in the last column together with the percentage weight of formic acid in the condensate. The experiments summarized in Table II show that the yields of all products decrease with the time of contact. This phenomenon finds an adequate explanation only in the assumption that the reaction exhibits an induction period. A more detailed consideration of Table II shows that the yields of various reaction products are not affected in the same way. The amount of carbon dioxide decreases most rapidly, then the carbon monoxide, while hydrogen and particularly the condensable substances diminish only very slightly in quantity. There appear to be two explanations of this specific influence of

TABLE II

EFFECT OF TIME OF CONTACT ON REACTION OF OXYGEN WITH ACETYLENE

Temp., °C.	Moles passed × 10^3 C_2H_2	O_2	Moles formed × 10^3 CO	CO_2	H_2	HCOOH + HCHO	HCOOH alone	Av. time of contact, sec.
278	8.9	8.9	0.38	0.10	0.065	0.44		200
278	8.9	8.9	0.57	.075	.082	0.57		
% of total carbon passed			2.67	.49		2.8		
278	17.8	17.8	0.13	.037	.035	0.44		100
278	17.8	17.8	.22	.048	.078	0.51		
% of total carbon passed			.49	.12		1.33		
278	35.6	35.6	.16	.0	.052	0.35		50
278	35.6	35.6	.12	.016	.013	0.33		
% of total carbon passed			.20	.01		0.48		
310	8.9	8.9	2.54	.54	.29	1.18		200
310	8.9	8.9	2.90	.61	.30		0.88 (50.3%)	
% of total carbon passed			15.3	3.0		6.7	4.9	
310	17.8	17.8	3.07	0.59	.29	1.72		100
311	17.8	17.8	4.78	0.66	.40		1.09 (52.4%)	
% of total carbon passed			11.0	1.81		4.8	3.1	
310	35.6	35.6	1.24	0.33	.18	1.89		50
313	35.6	35.6	1.62	.45	.21		0.95 (46%)	
% of total carbon passed			2.01	.55		2.65	1.33	

the time of contact: either the induction period is different for different products, or the analyzed reaction products are not all due to the primary reaction. If this latter assumption is accepted, one can deduce further that the condensable substances, and possibly hydrogen, are the first products of the oxidation (or decomposition) of acetylene, while carbon monoxide and dioxide result from secondary decompositions or oxidation of these products. Although on first glance the results at 310°, Table II, seem to differ greatly from those at 278°, in reality they agree quite well. At 310°, 30% of the acetylene reacts during the longest contact time, and since the reaction velocity depends strongly on the acetylene concentration (see below), the velocity must decrease during the reaction period owing to consumption of acetylene in the reaction. On further decrease of contact time to fifty seconds the influence of the induction period overweighs that of the consumption of acetylene, and a general decrease in the reaction velocity is observed. The data in Table II show that the yields of carbon monoxide and dioxide decrease more rapidly with the contact time than do the other reaction products; in fact, the yield of condensable substances even increases slightly.

A decrease in the contact time has little effect on the absolute amount and the weight concentration of formic acid. The increase in the total amount of oxidizable matter in the condensate shows that with decreasing contact time the amount of water present must decrease, whereas the aldehyde fraction must increase. Indeed, the iodine determination of aldehydes carried out on a sample obtained with fifty seconds' contact time yielded 30% of aldehydes in the condensate as compared with 9% obtained with 200 seconds' contact time.

The influence of gas composition on the reaction velocity was established by runs made with gases composed of 75% acetylene, 25% oxygen and 25% acetylene, 75% oxygen. These runs, which are presented in Table III, show that the reaction velocity falls off very rapidly with decreasing acetylene–oxygen ratio. The variation in reproducibility of the experiments makes uncertain any conclusions as to whether all reaction products decrease in this same ratio or not. The average decrease of two main products, carbon monoxide and the condensable matter, is about ten-fold for a change of composition from 75 acetylene–25 oxygen to 25 acetylene–75 oxygen, or a three-fold change of each of the reactants. This makes it probable either that the reaction velocity is proportional to the square of acetylene concentration, or that it is proportional to its first power and is retarded by oxygen. Runs were made with a gas mixture containing 25% acetylene and 75% oxygen in one case and 75% of air in the other case to decide between these two possibilities. These runs are presented in Table III, Series B, which shows that notwithstanding a five-fold change in oxygen concentration, the reaction velocity is not greatly changed. As a slight increase in the reaction velocity in the mixture containing air can be observed, it appears probable that oxygen has only a slight retarding influence. Accordingly, to account for the results given in Table III, one must assume that the reaction velocity is proportional to the square of the acetylene concentration and is very slightly retarded by oxygen.

Table III

Effect of Concentration of Reactants on Reaction of Oxygen with Acetylene

Average time of contact, 200 seconds

Series	Temp., °C.	Moles passed × 10^3			Moles formed × 10^3			
		C_2H_2	O_2	N_2	CO	CO_2	H_2	HCOOH + HCHO
A	278	13.35	4.45	...	1.34	0.233	0.14	1.100
	279	13.35	4.45	...	1.16	.244	.13	1.170
	277	4.45	13.35	...	0.12	.042	.02	0.095
	278	4.45	13.35	...	.07	.030	.02	.157
B	296	4.45	13.35	...	.39	.138	.04	.433
	296	4.45	2.67	1.068	.60	.112	.03	.485

To study the influence of the walls of the reaction vessel on the reaction velocity, a pyrex tube was filled with broken pyrex glass of a size between 6- and 14-mesh. The surface in this vessel was increased many-fold and the average diameter of the free spaces was reduced from 20 mm. in the open vessel to 1 mm. or less. Considerable difficulty was experienced at the beginning of these experiments from an inconstancy of the reaction velocity. Table IV presents two consecutive series of experiments and shows that a prolonged exposure of the vessel to the acetylene–oxygen mixture results in a decreasing reaction rate. An attempt to produce more constant conditions was made by treating the packed vessel with a normal solution of sodium chloride, washing once with distilled water, and drying. Pease[2] has observed in oxidation of other hydrocarbons using potassium chloride on glass that the salt treatment of the glass surface brought about a marked decrease in reaction velocity. Our treatment with sodium chloride did not have such an effect. The reaction velocity was speeded up slightly and was more reproducible. The absence of a lasting effect of sodium chloride is not astonishing because the glass surface in both the treated and untreated vessels became coated with a thin deposit of carbon, which was in contact with the acetylene–oxygen mixture. Table V presents the data obtained with the coated vessel and an equimolal mixture of acetylene and oxygen. The remarkable feature of the experiments is that they indicate a reaction velocity in the packed vessel many-fold slower than in the empty one. Thus at 315° some 30% of acetylene reacted in the empty vessel, whereas in the packed tube the reaction amounted to only 3 to 4%. At the same time the course of reaction is profoundly changed; the main products are now carbon dioxide and water. Increase in the amount of water in the reaction products was established by weighing the cooled trap before and after several runs. The change in the course of the reaction is manifest also from experiments on the influence of the time of contact and of the composition of the gas mixture on the reaction velocity. These data are presented in Table VI, Series A and B.

It is apparent from these experiments that the induction period characterizing the reaction in the unpacked vessel has disappeared. The velocity of reaction is now approximately independent of the time of contact and no distinct difference can be observed in the behavior of the various products of reaction. Accordingly there are no grounds to assume now that carbon monoxide and carbon dioxide are products of secondary reactions, as there were in the case of the unpacked vessel where the primary reaction led to the formation of "condensable substances." Series B, Table VI, shows the influence of the composition of the gas mixture on the reaction velocity. Variations in the compositions of the gas mixture leave the reaction velocity almost unchanged. Mixtures rich in acetylene show a somewhat higher

TABLE IV

DATA ON REACTION OF OXYGEN WITH ACETYLENE IN VESSEL OF 24-MM. INTERNAL DIAMETER PACKED WITH PYREX GLASS, 6- TO 14-MESH

Average time of contact, 200 seconds

Temp., °C.	Moles passed $\times 10^3$		Moles formed $\times 10^3$			
	C_2H_2	O_2	CO	CO_2	H_2	HCOOH + HCHO
256	8.9	8.9	0.110	0.22	0.020	0.0
280	8.9	8.9	.083	.25	.013	.030
315	8.9	8.9	.148	.42	.013	.045
338	8.9	8.9	.343	.93	.039	.081
355	8.9	8.9	.283	1.08	.043	.036
356	8.9	8.9	.435	1.30	.057	.126
335	8.9	8.9	.320	0.63	.043	.121
315	8.9	8.9	.410	.29	.043	.054
297	8.9	8.9	..	.22	..	.054
275	8.9	8.9	..	.05	..	.027
250	8.9	8.9	.048	.03	.009	.018

TABLE V

DATA ON REACTION OF OXYGEN WITH ACETYLENE IN VESSEL OF 24-MM. INTERNAL DIAMETER, PACKED WITH PYREX GLASS, 6- TO 14-MESH, AND TREATED WITH 1 NORMAL SODIUM CHLORIDE SOLUTION

Average time of contact, 200 seconds

Temp., °C.	Moles passed $\times 10^3$		Moles formed $\times 10^3$			
	C_2H_2	O_2	CO	CO_2	H_2	HCOOH + HCHO
256	8.9	8.9	0.04	0.02	0.02	0.01
277	8.9	8.9	.12	.04	.02	...
277	8.9	8.9	.05	.08	.02	...
297	8.9	8.9	.06	.12	.01	...
315	8.9	8.9	.10	.52	.01	.01
316	8.9	8.9	.10	.32	.01	...
337	8.9	8.9	.56	1.77	.06	.06
352	8.9	8.9	.74	2.70	.09	.05
354	8.9	8.9	.68	2.26	.08	.06

TABLE VI

EFFECT OF CONCENTRATION OF REACTANTS AND OF TIME OF CONTACT ON REACTION OF OXYGEN WITH ACETYLENE IN A CYLINDRICAL VESSEL OF 22-MM. INTERNAL DIAMETER PACKED WITH PYREX GLASS, 6- TO 14-MESH, AND TREATED WITH 1 NORMAL SODIUM CHLORIDE SOLUTION

Series	Temp., °C.	Moles passed × 10^3			Moles formed × 10^3				Av. time of contact, sec.
		C_2H_2	O_2	N_2	CO	CO_2	H_2	HCOOH + HCHO	
A	317	8.9	8.9	..	0.260	0.76	0.026	0.135	200
	316	8.9	8.9	..	.220	.56	.022	.063	
	316	17.8	17.8	..	.210	.62	.035	.140	100
	316	35.6	35.6	..	.305	.55	.052	.067	50
B	316	8.9	26.7	..	.148	.48	.017	.063	100
	316	8.9	26.7	..	.218	.54	.0	.036	
	316	26.7	8.9	..	.235	.54	.035	.166	100
C	316	8.9	5.3	21.4	..	.14	..	.018	100

rate, but the increase is much less than the ten-fold change observed in the unpacked vessel. This means that the reaction velocity is no longer proportional to the square of the acetylene concentration. The experiment of Series C, Table VI, in which a part of the oxygen was replaced by nitrogen, shows further that the rate, instead of being weakly inhibited by oxygen, now is more or less proportional to the oxygen concentration.

Discussion of Experimental Results

A comparison of the reaction rates in packed and unpacked vessels shows that the oxidation of acetylene under the conditions employed here is a homogeneous gas reaction. An increase in the glass surface does not increase the rate; instead, such an increase of the surface decreases the reaction rate many-fold. It has been shown by Pease,[2] Hinshelwood and Thompson,[13] and Semenoff[5] that this behavior characterizes chain reactions. The abnormal dependence on the concentration of the reactants is further evidence favoring the chain character of the reaction. Oxygen, which must enter the reaction mechanism, not only does not favor the reaction but even slightly inhibits it. Such behavior is incomprehensible from the point of view of classical chemical kinetics.

The analysis of the oxidation products shows glyoxal, formaldehyde and formic acid, aside from gaseous products. It is obvious that the formation of glyoxal must precede the formation of formaldehyde and formic acid in a stepwise oxidation. The change in the amounts of glyoxal, formaldehyde and formic acid with contact time demonstrates clearly the stepwise character of the oxidation which has already been suggested by Bone.[6] However, we do not consider his scheme correct in detail. Instead of a primary product containing two hydroxyl groups, a substance of the same total composition, $C_2H_2O_2$, but consisting of two aldehyde groups, namely glyoxal, is obtained.

[13] Hinshelwood and Thompson, *Proc. Roy. Soc.* (London), **118A**, 170 (1928).

There is a variety of possible reactions which glyoxal may undergo under our experimental conditions. Since reactions involving more than two molecules simultaneously are kinetically less probable than bimolecular and unimolecular processes, we can limit our discussion to the latter.

$$\text{CHO—CHO} \longrightarrow \text{CO} + \text{HCHO} \quad (1)$$
$$\text{CHO—CHO} \longrightarrow 2\text{CO} + \text{H}_2 \quad (2)$$
$$\text{CHO—CHO} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{HCOOH} \quad (3)$$
$$\text{CHO—CHO} + \text{O}_2 \longrightarrow \text{CO} + \text{O} + \text{HCOOH} \quad (4)$$
$$\text{CHO—CHO} + \text{O}_2 \longrightarrow \text{CO} + \text{CO}_2 + \text{H}_2\text{O} \quad (5)$$

Our experiments enable us to distinguish between the relative importance of these reactions. Reaction 3 certainly does not take place to any considerable extent, for otherwise a much larger relative yield of carbon dioxide would be obtained than was actually observed. Reaction 2 cannot be predominant because only small quantities of hydrogen were obtained throughout. On the other hand, the fact that the hydrogen yield decreased only slowly on decrease of the contact time makes it probable that it is this reaction and not a decomposition of formaldehyde or formic acid that produces hydrogen. Bone maintains that hydrogen in the reaction products is due to a reaction of the type, $\text{HCOOH} \longrightarrow \text{H}_2 + \text{CO}_2$, but our experiments point strongly against this inasmuch as they show that, on variation of the contact time, the yields of carbon dioxide and of hydrogen are quite different. Accordingly Reaction 2 may be considered as playing a secondary role in the reaction sequence. Bone attributes the formation of formic acid to a secondary oxidation of formaldehyde only. Our experiments are not conclusive enough to decide whether Reaction 4 or the process $\text{HCHO} + \text{O}_2 \longrightarrow \text{HCOOH} + \text{O}$ produces formic acid. In both cases one would expect decreasing yields of acid when the time of contact is decreased, but Reaction 4 would lead to a slower decrease than its formation in the oxidation of formaldehyde. A slight decrease in the amount of formic acid was actually observed; this might be construed as showing the occurrence of Reaction 4. A final decision will be possible only after a more detailed study of the yields of formic acid and formaldehyde.

The occurrence of Reaction 5 is also uncertain at present. The fact that the yields of carbon dioxide and water both decrease rapidly on shortening the contact time speaks in favor of our theory of the formation of these stable reaction products in some later stages of the reaction sequence, perhaps in the decomposition or oxidation of formic acid. The origin of carbon monoxide in the reaction is probably due to several processes. Its main source, especially at the lower temperatures, is Reaction 1. At higher temperatures additional sources of carbon monoxide may be the reactions

$$\text{HCHO} \longrightarrow \text{H}_2 + \text{CO}$$
$$\text{HCOOH} \longrightarrow \text{CO} + \text{H}_2\text{O}$$

The experiments in the packed vessel show that an increase in the glass surface changes the kinetics and the entire course of the reaction. It appears that a heterogeneous oxidation of acetylene directly to carbon dioxide and water, which was quite subordinate in the unpacked vessel, has been sufficiently accelerated to overshadow the homogeneous reaction. The fact that the glass surface has a profound influence on the yield of carbon dioxide is in favor of this explanation.

A problem which remains to be discussed is the coördination of the chemical side of the processes involved in the oxidation of acetylene with the chain character of the reaction and with the kinetic relations observed. Since none of the reactions are reversible under the experimental conditions and glyoxal appears in only small quantities, it must be the primary process of oxidation of acetylene that is the rate-determining process, namely, $C_2H_2 + O_2 = C_2H_2O_2$.

Accordingly one would expect the reaction rate to be proportional to the product of the concentration of acetylene and oxygen, but this is not the case. The reaction rate is proportional to the square of the acetylene concentration and is practically independent of oxygen. Furthermore, the reaction exhibits an induction period. Similar characteristics have been observed by Thompson and Hinshelwood[4] in the oxidation of ethylene. These authors' explanation of the reaction order is essentially this: a molecule resulting from addition of oxygen to ethylene will collide with a molecule of either ethylene or oxygen; the collision with ethylene is favorable to the propagation of a reaction chain while the collision with oxygen puts an end to further chemical processes. This scheme expressed kinetically yields the experimental order. Our results with acetylene can be interpreted in the same manner. The formation of glyoxal, being an addition reaction, must take place through a three-body collision.[14] A formal agreement with experiment is obtained if it is assumed that only with acetylene as the third body is glyoxal formed, while the action of oxygen is different. It is astonishing that glyoxal is formed at all as a primary product because the direct formation of carbon monoxide and formaldehyde, $C_2H_2O_2 = CO + HCHO$, being also highly exothermic, does not need a three-body collision and therefore should occur much more readily.

The presence of reaction chains has been shown, but their mechanism remains at present uncertain. The deduction can only be made from the existence of the induction period that the presence and further oxidation of intermediary products speed up the primary oxidation of acetylene. It is quite possible that free oxygen atoms resulting in some of the single reaction steps discussed above play an important role in the reaction.

Summary

Experiments are described that show that the thermal oxidation of acetylene by oxygen can be conveniently studied in pyrex vessels between

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[14] Born and Franck, *Z. Physik*, **31**, 411 (1925).

250 and 315°. A comparison of the reaction rates in packed and unpacked vessels shows not only that the reaction is homogeneous but that it is of the chain type.

The change in composition of the condensable reaction products with time of contact shows that the oxidation proceeds through the stages glyoxal–formaldehyde–formic acid. The gaseous products consist mainly of carbon monoxide, together with carbon dioxide and hydrogen. A study of the change in gas composition with contact time indicates that carbon monoxide originates mainly from the direct decomposition of glyoxal, and that carbon dioxide is due to oxidation or decomposition of formic acid, whereas the origin of the traces of hydrogen is at present uncertain.

The velocity of reaction is proportional to the square of the acetylene concentration and is independent of the oxygen concentration.

In packed vessels the homogeneous oxidation is almost entirely suppressed, and a heterogeneous oxidation of acetylene on the glass surface directly to carbon dioxide and water takes place. The rate is roughly proportional to the first power of the acetylene and oxygen concentrations. The mechanism of the reaction has been discussed.

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A MAGNETO-OPTIC METHOD OF CHEMICAL ANALYSIS

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This paper reports some results of a method which promises to be of value as a new means of chemical analysis. It also suggests a new angle of approach to certain aspects of the problem of ionization in liquids. The method is a refinement of one previously described by Allison[1] in the investigations of the time lag differences of the Faraday effect behind the magnetic field in certain liquids as a function of the wave length of the light used.

In a study of solutions it was subsequently found that each chemical compound, regardless of the presence of other substances, produces its characteristic minimum (or minima) of light intensity, which persists until the concentration is reduced to about 1 part in 10^{11}.[2] This fact suggested that the method might have application in some cases of chemical analysis.

The authors[3] have extended these findings of Allison to include a rather comprehensive series of solutions of chlorides, nitrates, sulfates and hydroxides.

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[1] Allison, *Phys. Rev.*, **30**, 66 (1927).

[2] Allison, *ibid.*, **31**, 313 (1928).

[3] Allison and Murphy, *ibid.*, **35**, 124 (1930).