2.   The reaction is rather powerfully inhibited by oxygen.

3.   Without added oxygen, the rate of chlorination appears to be proportional to the product of the concentrations of methane and chlorine. In presence of oxygen the rate is more nearly proportional to the square of the chlorine concentration, independent of the methane concentration, and inversely proportional to the oxygen concentration.

4.   The kinetics resemble that of the photochemical hydrogen-chlorine reaction.   If the mechanism is the same, a thermal dissociation of chlorine would seem to be involved.   Approximate calculations indicate that this can hardly proceed at a sufficient rate to give the observed reaction rate.

PRINCETON, NEW JERSEY

THE REACTION BETWEEN OXYGEN AND ETHYLENE.   I

BY SAMUEL LENHER

The oxidation of ethylene has been a subject of study for many years.[1] The present rather comprehensive investigation was undertaken with the object of studying the mechanism of the slow thermal oxidation of the olefins.   The olefins offer a specific point of attack by oxygen at the carbon–carbon double bond, and as ethylene has but one such bond study of the oxidation of ethylene promised to throw light on the problem of the addition of oxygen at a simple olefin linkage, and accordingly to give data which could be applied generally to the oxidation of the mono-olefin hydrocarbons.

Especial attention was directed in the present work to the identification of the intermediate oxidation products, for the course of the oxidation can only be determined by analysis of all the products of the reaction.   Bone and R. V. Wheeler[1c] found that formaldehyde was the most prominent intermediate oxidation product and that its formation preceded that of carbon oxides and steam.   They concluded that the reaction took place in a series of steps, and postulated the formation of vinyl alcohol and a hypothetical dihydroxyethylene as primary steps preceding the appearance of formaldehyde.   The occurrence of carbon oxides and water was the final stage involving the decomposition and oxidation of formic acid which was derived from formaldehyde.   Later, Blair and T. S. Wheeler[1e] showed that acetaldehyde was an oxidation product of

[1] (a) Schützenberger, *Bull. soc. chim.*, **31**, 482 (1879);   (b) Phillips, *Trans. Am. Phil. Soc.*, **17**, 149 (1893);   (c) Bone and R. V. Wheeler, *J. Chem. Soc.*, **85**, 1637 (1904); (d) Willstätter and Bommer, *Ann.*, **422**, 36 (1920);   (e) Blair and T. S. Wheeler, *J. Soc. Chem. Ind.*, **41**, 303T (1922); **42**, 415T (1923);   (f) Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), A**125**, 277 (1929).

the slow combustion of ethylene, and in one experiment lasting ninety hours they found that half the ethylene consumed was converted to acetaldehyde. Willstätter and Bommer[1d] observed that at temperatures of 500–600° in addition to formaldehyde the thermal decomposition of ethylene became a principal reaction. Recently, Thompson and Hinshelwood[1f] in a study of the kinetics of the reaction have shown that the rate of reaction is approximately third order, the rate depending much more on the partial pressure of ethylene than of oxygen. They concluded that the reaction follows a chain mechanism, the chains being propagated by the collision of an unstable peroxide molecule formed initially from ethylene and oxygen with ethylene, forming hydroxylated molecules, which continue the chain.

Experimental

Small-Scale, One-Pass Experiments.—The reaction was first studied by the flow method at atmospheric pressure. Ethylene (United States Industrial Chemical Co.) from a commercial cylinder made by the dehydration of ethyl alcohol was dried with calcium chloride and used without further purification. The analysis of the ethylene was 98.2% ethylene, 0.2% saturated hydrocarbons, and the remainder air. Tank oxygen (Air Reduction Co.) dried with sulfuric acid was used. The gases at regulated rates of flow were mixed in a capillary at the entrance to the reaction vessel. The Pyrex cylindrical reaction vessel, 20 mm. in diameter, was heated in an electric tube-furnace. Temperatures were read by means of a chromel–alumel thermocouple in a thin-walled glass tube in the center of the vessel.

The gases leaving the furnace passed through a U-tube cooled in solid carbon dioxide, and a spiral wash-bottle containing a solution of standardized barium hydroxide to absorb carbon dioxide quantitatively, and were collected in a water gasometer. The gas analyses were carried out as described by Kistiakowsky and Lenher.[2] The amount of the condensable products was determined by weighing.

Table I summarizes the results of experiments with equal volumes of ethylene and oxygen in a 65-cc. vessel. The main products were the condensable matter and carbon monoxide. Less important products were carbon dioxide and hydrogen.

It is clear from Table I that temperature has a strong influence on the reaction velocity; the amount of carbon monoxide increases two- to threefold for a 20° increase in temperature. The amount of condensable products increases more slowly as it is not quite doubled for a 20° temperature increase. Above 400° the condensable matter actually decreases, due to secondary decompositions which will be considered later. The reproducibility of the experiments in Table I is interesting in view of the chain nature of the reaction,[1f,3] which in general tends to cause variable results.

The condensate was found to contain ethylene oxide, ethylene glycol, glyoxal, formaldehyde, formic acid and water. The presence of formaldehyde was shown by the Schiff's reagent test, by the formation of the

[2] Kistiakowsky and Lenher, THIS JOURNAL, **52**, 3785 (1930).

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

TABLE I

EFFECT OF TEMPERATURE ON REACTION OF OXYGEN WITH ETHYLENE

360 cc. of 1 ethylene : 1 oxygen mixture·used.   Average time of contact, 75 seconds

Temp., °C.	Condensable matter, g.	Reaction products		
		CO, cc.	CO$_2$, cc.	H$_2$, cc.
360	0.0534	16.8	2.7	. . .
360	.0536	20.3	2.4	1.5
360	.0580	19.1	2.6	0.4
370	.0706	27.5	3.8	0.2
370	.0709	24.5	3.9	0.3
380	.0927	. . . .	5.8	. . .
380	.0905	39.8	5.5	1.1
380	.0960	40.2	5.3	1.3
390	.1341	67.9	9.5	4.8
390	.1483	. . . .	9.8	. . .
390	.1342	74.1	8.8	3.7
400	.1689	102.5	11.4	2.9
400	.1666	106.0	10.7	4.1
410	.1524	122.7	14.0	10.7
410	.1506	137.2	13.4	13.4

characteristic yellow *p*-nitrophenylhydrazone, and by its characteristic smell.   Formic acid was identified by the mercuric oxide test.   Ethylene glycol was identified by preparing the crystalline ethylene glycol dibenzoate, m. p. 71°.   The presence of glyoxal was shown by the formation of the characteristic brick red di-*p*-nitrophenylhydrazone and the Bamberger test for the di-*p*-nitrophenylhydrazone of glyoxal.   No evidence was obtained for the presence of acetaldehyde, glycolic aldehyde, glycolic acid or oxalic acid.

Ethylene oxide was identified using the saturated magnesium chloride solution test,[4] and an improvement on this test.   This test is based on the property of ethylene oxide of adding inorganic acids directly to its molecule.[5]   In the case of the halides of aluminum and the divalent halides of magnesium, iron, tin, zinc and manganese in neutral solution, ethylene oxide absorbs the acid radical freed by dissociation and hydrolysis, and the metallic hydroxide is precipitated.   The appearance of a precipitate in a controlled test solution is evidence of the presence of ethylene oxide.   The sensitivity of the test depends directly on the solubility product of the hydroxide liberated, the reaction being expressed as

$$MnCl_2 + 2 \genfrac{}{}{0pt}{}{CH_2}{CH_2}\!\!\Big\rangle O + 2H_2O \longrightarrow 2 \genfrac{}{}{0pt}{}{CH_2OH}{CH_2Cl} + Mn(OH)_2$$
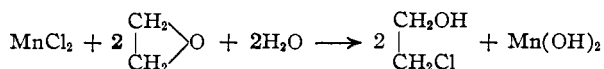
[4] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1905, Vol. I, p. 160.

[5] Walker, *Ber.*, **34**, 4115 (1901).

The hydroxides of zinc, divalent iron, tin and manganese are all more insoluble than magnesium hydroxide, and their chlorides can give a more sensitive test for ethylene oxide than màgnesium chloride, which is recommended in the literature. Numerous tests showed that a saturated neutral solution of manganous chloride ($MnCl_2$) gives the best test for ethylene oxide (i. e., the test which is most sensitive and easy to control).

The influence of the concentration of the reactants on the velocity of the oxidation of ethylene was established using mixtures of 3 ethylene: 1 oxygen, 3 oxygen : 1 ethylene and 1 ethylene : 1 air. Thompson and Hinshelwood[1f] have shown that at 400–480° and total pressures of 150 to 400 mm. the rate of reaction is proportional to the third power of the ethylene concentration. The experiments in Table II agree very well with their results.

TABLE II

EFFECT OF CONCENTRATION OF REACTANTS ON REACTION OF OXYGEN WITH ETHYLENE

360 cc. gas mixture used. Average time of contact, 75 seconds

Temp., °C.	Composition of reacting gases, %		Condensable matter, g.	Reaction products		
	O_2	C_2H_4		CO, cc.	CO_2, cc.	H_2, cc.
350	25	75	0.0874	27.6	2.6	0.6
350	25	75	.0836	30.7	3.5	0.9
350	0.0	100	.0039	0.0	0.0	0.0
360	25	75	.1184	47.0	4.5	3.8
360	25	75	.1167	44.5	4.3	4.3
360	25	75	.1221	46.4	4.5	4.1
370	75	25.	.0064	1.0	0.0	0.0
370	75	25	.0055	1.6	0.0	0.0
370	25	75	.1268	50.9	4.8	6.2
370	25	75	.1125	45.2	4.2	5.7
370	25	75	.1201	...	4.8	...
390	75	25	.0162	7.5	0.9	0.3
390	75	25	.0142	4.6	0.9	0.3
390	50	50	.1342	67.9	9.5	4.8
390	10.5[a]	50	.0530	23.8	2.4	1.6
390	10.5[a]	50	.0485	18.5	3.4	1.5

[a] Air used in these experiments.

The experiments at 370° in Table II show a twenty-fold variation in the yield of products for a three-fold variation in concentration of the reactants. These data suggest that the reaction velocity is proportional to the cube of the ethylene concentration, or that it is proportional to a higher power and is retarded by oxygen. To examine these two possibilities, runs were made with a gas mixture containing 50% ethylene and 50% air in one case and 50% oxygen in the other. Comparison of these experiments in Table II shows that reducing the oxygen concentration five-fold brings about a decrease of about three-fold in the amount of the

several reaction products. This result cannot be taken quantitatively, for analysis of the gases from the runs with air showed that all the oxygen was consumed. This may mean that a lack of sufficient oxygen to enter into reaction with ethylene brought about the apparent decrease in the rate of reaction. However, it can be concluded that while oxygen in excess is not favorable to rapid reaction rates, its retarding influence, if it is real at all, is very slight. The unfavorable action of oxygen may be simply that of an inert diluent like nitrogen. The results given in Table II are accounted for on the assumption of Hinshelwood and Thompson that the rate of reaction of ethylene with oxygen is proportional to about the third power of the ethylene concentration and is practically independent of oxygen. The small amount of condensable matter obtained in the experiment at 350° with pure ethylene in Table II, which proved to be water, showed that the thermal polymerization of ethylene plays no part in these experiments.

The influence of the time of contact on the reaction was studied with a 1 ethylene : 1 oxygen mixture at different rates of flow. The results of these experiments at 380° are given in Table III.

TABLE III

EFFECT OF TIME OF CONTACT ON REACTION OF OXYGEN WITH ETHYLENE

360 cc. 1 ethylene : 1 oxygen mixture used. Temperature, 380°

Average time of contact, seconds	Condensable matter, g.	Reaction products		
		CO, cc.	CO_2, cc.	H_2, cc.
150	0.1575	93.8	13.1	2.5
150	.1617	98.1	13.3	2.7
75	.0905	39.8	5.5	1.1
75	.0960	40.2	5.3	1.3
43	.0282	10.7	1.2	0.7
43	.0414	10.2	1.7	0.5

These experiments show that the yield of all the products decreases with the time of contact, and indicate the existence of an induction period in the reaction, which is characteristic of hydrocarbon oxidations. It is evident that the several reaction products are not all affected in the same way. With increasing flow the amount of carbon monoxide falls off most rapidly, followed by the carbon dioxide, the condensable products and hydrogen.

The effect of the walls of the vessel was investigated using a cylindrical Pyrex tube packed with fragments of Pyrex glass of size 4-mesh. The volume of the packed tube was 28 cc. The average diameter of free space in the packed tube was 1–2 mm. while in the unpacked reaction vessel it was 20 mm. The rate of flow was adjusted to make the time of contact approximately that in the experiments with the empty vessel; at 525°, the average time of contact was sixty-six seconds. Table IV gives the results of experiments with the Pyrex glass packed vessel.

TABLE IV

REACTION OF OXYGEN WITH ETHYLENE IN VESSEL PACKED WITH PYREX GLASS, 4-MESH

360 cc. 1 ethylene : 1 oxygen mixture used.   Average time of contact, 66 seconds

Temp., °C.	Condensable matter, g.	Reaction products		
		CO, cc.	CO_2, cc.	H_2, cc.
450	....	..	..	..
500	0.0048	5.5	1.6	1.6
520	.0166	6.6	5.1	0.9
540	.0718	52.0	11.5	3.9
550	.1028	81.2	17.0	6.4

These experiments show that the rate of reaction in the packed vessel was many-fold slower than in the experiments using the empty vessel given in Table I.   In the unpacked vessel at 390°, 70% of the ethylene reacted and at 410°, 90% of the ethylene was consumed, while in the packed vessel no reaction could be detected at 450° and the rate of reaction became measurable only above 500°.   The reaction which did take place proceeded to the end-products of reaction under the influence of the surface.   The principal products of the reaction in the packed vessel were the oxides of carbon and water.   The condensable matter appeared to be almost entirely water; it gave a weak qualitative test for aldehydes and contained a small amount of formic acid.   None of the other intermediate oxidation products were detected.   The decrease in the rate of reaction on increasing the exposed surface in these experiments and in the experiments of Thompson and Hinshelwood indicates the existence of reaction chains which are stopped by the surface.   The pronounced retardation by increased surface may be due to two effects: first, the effect of the surface in preventing the slow reaction between oxygen and ethylene and, second, the effect of the surface in catalyzing the oxidation of ethylene to the end-products of reaction in a single step without the formation of reaction chains.   In these experiments the oxidation of ethylene does not take place, or it proceeds to completion at the surface.

The effect of gas-phase oxidation catalysts on the reaction was studied in a number of experiments using nitric acid vapor and nitrogen oxides. If the action of nitrogen oxides is catalytic, it must be that of an active oxygen carrier which is alternately reduced in the reaction to nitric oxide and oxidized by oxygen, and is not destroyed in the process.[6]   Experiments at 300 to 400° using a 1 ethylene : 1 oxygen mixture with 3 to 5% by volume of nitric acid vapor (and its decomposition products) showed that nitrogen oxides did not have any marked effect on the reaction, that is, the temperature range of the slow oxidation reaction was not lowered appreciably nor was the actual amount of oxidation at one temperature greatly increased in the presence of nitrogen oxides.   The possible catalysis of the oxidation by nitrogen oxides was tested by investigating the

        [6] Lenher, THIS JOURNAL, 53, 2962 (1931).

reaction between nitric oxide and ethylene. An equimolecular mixture of ethylene and nitric oxide free of other nitrogen oxides and oxygen was passed through a reaction vessel at 295° with a time of contact of eighty seconds, and the reaction products collected as described above. The products condensed at −78° were nitrogen trioxide (N_2O_3), a clear liquid, and ice; the gaseous products were carbon monoxide, carbon dioxide and nitrogen. The liquid product gave a strong test for aldehyde with Schiff's reagent and gave a heavy brick-red precipitate mixed with a yellow precipitate on adding a solution of p-nitrophenylhydrazine acetate, showing the presence of glyoxal and formaldehyde. The red di-p-nitrophenylhydrazone of glyoxal gave a blue coloration with alcoholic potash characteristic of a positive Bamberger test. This experiment showed that ethylene reacts chemically with nitric oxide at 295°; that is, ethylene reduced nitric oxide to lower oxides and elementary nitrogen with the formation of oxidation products of ethylene. Thus the action of nitrogen oxides is not catalytic under these conditions, for ethylene reduces the oxides of nitrogen beyond the stage of nitric oxide, and reoxidation to a higher oxide cannot take place.

It is interesting to note in this connection that in the oxidation of the three typical hydrocarbons methane,[7] ethylene and acetylene[6] in the presence of nitrogen oxides, the oxidation of acetylene is the only one in which the nitrogen oxides are not consumed chemically. In these reactions methane is oxidized to formaldehyde, and ethylene is oxidized to glyoxal and formaldehyde, which indicates that these oxidations take place with dehydrogenation of the hydrocarbon and reduction of the nitrogen oxide. Acetylene, however, is oxidized to glyoxal without dehydrogenation. These observations afford qualitative evidence of the different energies of separation of the C–H bonds in the simple aliphatic hydrocarbons. In methane two of the hydrogens can be removed with oxygen or nitrogen oxides leaving a CH_2 residue which goes to formaldehyde; in ethylene one hydrogen can be removed from each carbon atom leaving a C_2H_2 residue which is oxidized to glyoxal and formaldehyde, but in acetylene the C–H bindings are so strong that they cannot be broken directly by oxygen or nitrogen oxides, and glyoxal is formed.

Larger-Scale, One-Pass Experiments.—In order to obtain more accurate data on the nature of the intermediate products of the reaction between ethylene and oxygen, the reaction was studied by the flow method using larger quantities of the reactants. The metered gases, taken from commercial cylinders and thoroughly mixed, were passed through a reaction vessel heated in an electric tube furnace. The vessels used were 5.5 cm. in diameter and 40 cm. long with 20 mm. inlet and outlet tubes at the ends. Vessels made of Pyrex glass, fused quartz, stainless steel and aluminum were used. A thermocouple well entered the vessel through the inlet tube along the axis. Temperatures were read and controlled by means of two chromel–alumel thermocouples

[7] Smith and Milner, *Ind. Eng. Chem.*, **23**, 375 (1931).

(cold junctions at $0°$), one of which operated an Engelhardt temperature controller. The reacted gases passed through two traps in series cooled in ice, and a simple trap and a long spiral trap cooled with solid carbon dioxide–methanol mixture to remove condensable products. Samples of gas were analyzed frequently during a run. The aldehyde content of the products was determined by the familiar bisulfite–iodine titration. As occasional qualitative tests showed the presence of no aldehydes other than formaldehyde in these experiments the aldehyde content was calculated as formaldehyde. The formaldehyde was condensed as trioxymethylene, $(CH_2O)_3$. The acid products, which will be considered in detail below, were determined by titration with standard alkali.

Ethylene oxide, which was recovered in the traps cooled with solid carbon dioxide, was estimated by conversion to glycol with dilute phosphoric acid in pressure bottles and fractionation in a still with a 75-cm. air-jacketed column. The distillate was analyzed for aldehyde and acid. The theoretical conversion factor for ethylene oxide to glycol is 1.41 and for ethylene oxide to diethylene glycol it is 1.20. Experiments on the hydration of pure ethylene oxide to glycol gave the conversion factor of 1.285, which was used.

The formation of saturated hydrocarbons or of higher olefins appeared to play no important part in the reaction in large and in small vessels under the conditions discussed in this part of the paper.

The marked influence of the walls of the vessel on the course of the reaction is shown by the data in Table V and Table VI. The reaction was

TABLE V

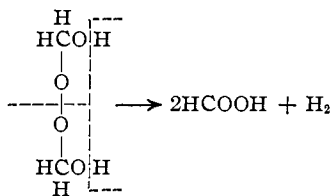REACTION OF OXYGEN WITH ETHYLENE IN 960-CC. VESSELS IN A ONE-PASS SYSTEM

						Compn. of gas, %				Liquid product, g.		
	85 parts ethylene : 15 parts oxygen	Time of contact, sec.	Temp., °C.	C_2H_4 oxidized, g.	C_2H_4	O_2	CO + H_2	CO_2	HCHO	HCOOH	$(CH_2)_2O$	
Expt.	Vessel used											
22	Pyrex	27	365	33.65	87.7	1.3	10.3	0.3	7.4	27.8	6.7	
26	Pyrex, 3% steam in gases	27	365	34.00	81.0	0.1	17.9	1.0	8.5	9.5	7.3	
27	Pyrex, 3% steam in gases	27	350	30.95	86.9	4.0	8.6	0.5	7.2	19.5	6.5	
29	KCl coated on Pyrex	27	365	31.45	87.8	2.7	7.7	1.8	18.7	0.8	6.3	
33	Stainless steel	22	365	15.79	85.5	6.5	5.6	2.4	14.1	.6	1.3	
35	Aluminum	30	365	18.80	86.6	3.5	7.9	2.0	3.9	.5	0.0	
36	K_2SiO_3 coated on Pyrex	27	365	17.84	86.3	7.9	3.5	2.3	12.7	.03	2.8	
39	Fused silica	27	365	32.15	86.5	2.0	9.6	1.9	18.8	4.15	5.9	

TABLE VI

YIELDS OF PRINCIPAL PRODUCTS IN ONE-PASS SYSTEM EXPERIMENTS ON ETHYLENE OXIDATION

Expt.	Vessel used	Per cent. of total C_2H_4 passed which is consumed	Per cent. CO, CO_2 and H_2	C_2H_4 consumed which goes to		
				HCHO	$(CH_2)_2O$	HCOOH
22	Pyrex	9.8	51.2	10.2	13.7	24.8
26	Pyrex, 3% steam in gases	9.9	65.0	11.6	14.7	8.5
27	Pyrex, 3% steam in gases	9.0	55.5	10.8	14.4	19.2
29	KCl coated on Pyrex	9.1	58.0	27.7	13.5	0.8
33	Stainless steel	4.6	52.0	41.8	5.1	1.1
35	Aluminum	5.5	89.8	9.6	0.0	0.8
36	K_2SiO_3 coated on Pyrex	5.4	58.6	31.7	9.7	.0
39	Fused silica	9.3	57.0	27.1	11.7	4.3

studied using high hydrocarbon concentrations, which were favorable to a rapid rate of reaction. In these large vessels it was necessary to use gas mixtures outside the explosion limits. The flow of gas was adjusted to give an average time of contact of twenty-seven to thirty seconds for the 960 cc. vessels at the temperature of reaction.

The formic acid in these experiments was formed from a product of the reaction which was found to be dioxymethyl peroxide, $CH_2OHOOCH_2OH$. The reaction products condensed in the ice traps, which will be called the ice condensate, evolved a gas slowly and continuously for days on standing at room temperature. This gas was pure hydrogen, and the hydrogen evolution was accompanied by a corresponding increase in acidity. For every mole of hydrogen evolved, two moles of formic acid was liberated. Analysis of the condensate showed a high content of formaldehyde and formic acid. On slightly warming the condensate, a highly exothermic decomposition took place which in some instances raised the solution to its boiling point; this decomposition was accompanied by a copious evolution of hydrogen. The decomposition was catalyzed by alkalies, yielding formates and hydrogen. The condensate freed iodine from potassium iodide, and in general exhibited the characteristics of a peroxide. On addition of ammonia oxygen was evolved with a small amount of hydrogen. Heating with excess lead oxide (PbO) gave lead formate with the evolution of a gas composed of two parts hydrogen and one of oxygen. These remarkable properties correspond to the behavior of dioxymethyl peroxide.[8] The formation of formic acid on titration with alkali takes place according to the equation

$$
\begin{array}{c}
\text{H} \\
\text{HCO} \bar{\text{H}} \\
| \\
\text{O} \\
\text{O} \\
| \\
\text{HCO} \bar{\text{H}} \\
\text{H}
\end{array} \longrightarrow 2HCOOH + H_2
$$

The total acidity of the free formic acid and of dioxymethyl peroxide was determined, after tests, by bringing a diluted sample rapidly to the boil-

[8] Dioxymethyl peroxide was discovered by Legler, in the slow oxidation of ether, *Ann.*, **217**, 381 (1883), and in the action of ozone on ethylene (*Jahresb. K. Chem. Centr.-Stelle öff. Ges. Pfl. Dresden*, 88–95 (1888); *Chem. Zentr.*, 1604 (1888)). Nef, *Ann.*, **298**, 202 (1897), and Baeyer, *Ber.*, **33**, 2479 (1900), discussed the structure of this compound and assigned it the formula, $HOCH_2OOCH_2OH$. It is probably identical with an unusual compound prepared by Fenton, *Proc. Roy. Soc.* (London), **A90**, 492 (1914), from formaldehyde and hydrogen peroxide which he called dimethylenediol peroxide or diformal peroxide hydrate. This compound is presumably the intermediate formed in the determination of formaldehyde with hydrogen peroxide and alkali; Blank and Finkenbeiner, *Ber.*, **31**, 2979 (1898); Wieland and Wingler, *Ann.*, **431**, 301 (1923); Rieche, "Alkylperoxide and Ozonide," Theodor Steinkopff Verlag, Dresden und Leipzig, 1931, p. 16.

ing point in a loosely stoppered flask and allowing it to boil for a few seconds to decompose the peroxide; the sample was then cooled and titrated at room temperature with standard alkali. The acid could not be determined by addition of excess alkali and back titration, or by titrating while hot, because of the Cannizzaro reaction with the formaldehyde in the sample.

The origin of dioxymethyl peroxide in the oxidation of ethylene seemed difficult to understand, for neither ethylene nor formaldehyde can give a compound of the composition of dioxymethyl peroxide, $C_2H_6O_4$, on direct oxidation with oxygen. The only active oxidizing agents which could yield dioxymethyl peroxide on reaction with ethylene, formaldehyde or ethylene oxide were ozone, hydrogen peroxide or atomic oxygen. The action of ozone presented kinetic difficulties, for it would be necessary to assume a hydrating action of ozone as well as an oxidizing action to give dioxymethyl peroxide. Atomic oxygen was ruled out for lack of any evidence for the existence of free oxygen atoms produced thermally and because atomic oxygen is known to oxidize the unsaturated hydrocarbons directly to carbon oxides and water.[9] The products of the reaction of oxygen with ethylene were tested for the presence of ozone and hydrogen peroxide. The reacted gases were bubbled through test solutions on issuing from the reaction vessel, and the products of reaction were also collected in ice-cooled traps and examined. The tests used were those recommended by Keiser and McMaster[10] and Mellor[11] for the detection of hydrogen peroxide and ozone, and were the titanium sulfate test of a brown color with hydrogen peroxide, the chromic acid and ether test of a blue color in the ether layer with hydrogen peroxide, the ferric chloride and potassium ferricyanide test of Prussian blue formation with hydrogen peroxide, the potassium iodide–starch test of a blue color with ozone or hydrogen peroxide, the test of benzidine in alcohol which gives a brown color with ozone, and the guaiacum tincture test of a blue color with hydrogen peroxide. The tests were carefully controlled with blanks using aliphatic and aromatic peroxides, formaldehyde, formic acid, and ethylene oxide, and hydrogen peroxide itself. The most sensitive test for hydrogen peroxide, that of a blue color with guaiacum tincture sensitized with diastase,[12] was found to be inapplicable to the test of the reaction products because of the interference of formaldehyde and formic acid, which reacted to mask the blue color test. No evidence was found for the presence of ozone in detectable amounts in the products. The reacted gases gave

[9] Harteck and Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

[10] Keiser and McMaster, *Am. Chem. J.*, **39**, 96 (1908).

[11] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1927, Vol. I, p. 951.

[12] Schönbein, *J. prakt. Chem.*, [1] **105**, 219 (1867); Lintner, *ibid.*, [2] **34**, 378 (1886); Schöne, *Z. anal. Chem.*, **33**, 155 (1894).

strong tests for hydrogen peroxide. The cold fresh ice condensate from the reaction gave a deep blue color in the ether layer in the chromic acid–ether test, an immediate brown color appeared with titanium sulfate, Prussian blue was formed in a solution of ferric chloride–potassium ferricyanide, and iodine was freed from potassium iodide, which showed the presence of hydrogen peroxide.

After the ice condensate had been kept in a refrigerator for four days, no test for hydrogen peroxide with chromic acid–ether was obtained, although a brown color with titanium sulfate appeared after ten minutes; addition of alkali caused the evolution of hydrogen and the development of acidity, which showed that dioxymethyl peroxide was still present. It was concluded that the hydrogen peroxide originally present had reacted with the formaldehyde on standing[13] with the formation of dioxymethyl peroxide. These tests showed that hydrogen peroxide was a product of the reaction between oxygen and ethylene, and indicated that dioxymethyl peroxide and formic acid might be formed from the reaction between formaldehyde and hydrogen peroxide.

The data in Tables V and VI show how the rate of the reaction and the course of the reaction depend on the nature of the walls of the reaction vessel. In Pyrex vessels dioxymethyl peroxide is a principal product, while in a silica vessel its amount is less than one-sixth of that in a Pyrex vessel, and in steel and aluminum vessels and vessels coated with potassium chloride and with potassium silicate its formation is entirely suppressed. When the formation of dioxymethyl peroxide and formic acid is reduced there is an increase in the amount of formaldehyde. In all the vessels except iron and aluminum the percentage of ethylene which is oxidized to ethylene oxide remains the same, although the total amount of the ethylene oxidized varies two-fold between the Pyrex vessel and the potassium silicate coated vessel. The smallness of the amounts of ethylene oxide formed in the metal vessels may be due either to a suppression of the reaction forming ethylene oxide or to a catalytic rearrangement of ethylene oxide on the walls to acetaldehyde,[14] which in turn is oxidized and decomposed to formaldehyde and formic acid.

In the experiments with a Pyrex vessel the condensates contained a sharp-smelling, light yellow oil of specific gravity less than 0.9. This oil boiled over the range 40 to 125°, leaving a residue which decomposed on further heating. It was soluble in alcohol and gave milky solutions with carbon tetrachloride, benzene and ether, and was insoluble in water. The oil was highly unsaturated and was slightly acidic in character; it was thought that the oil contained unsaturated compounds of an acetal-like nature.

13 Fenton, *Proc. Roy. Soc.* (London), A90, 492 (1914).

14 Ipatiev and Leontovitsch, *Ber.*, 36, 2016 (1903); Nef, *Ann.*, 335, 197 (1904).

Oxidation of Ethylene Oxide.—A mixture of 15 parts ethylene oxide vapor from a commercial cylinder (Carbide and Carbon Chemicals Corporation) and 85 parts oxygen was passed through a Pyrex glass vessel at 365° with a time of contact of twenty-seven seconds. No oxidation or decomposition of ethylene oxide to liquid or gaseous products was detected. It was concluded that ethylene oxide was stable in the presence of oxygen under the conditions of these experiments. The stability of ethylene oxide indicated that there were at least two principal reactions in the oxidation of ethylene, one reaction yielding ethylene oxide, and a second reaction between oxygen and ethylene forming formaldehyde, dioxymethyl peroxide and the other products.

Oxidation of Propylene.—The slow thermal oxidation of propylene was studied using a one-liter Pyrex vessel. A mixture of 85 parts propylene (Matheson Company) and 15 parts oxygen was reacted at 315° with a time of contact of thirty seconds. Reaction began at 280° but did not proceed rapidly below 300°. The products condensed in ice traps showed the presence of considerable amounts of a peroxide compound which decomposed with the evolution of hydrogen on warming or on addition of alkali, and which was assumed to be analogous to dioxymethyl peroxide. Tests on the condensate showed that the liquid products of the reaction were propylene oxide, propylene glycol, propionaldehyde, acetic acid, acetaldehyde, formic acid, formaldehyde and the peroxide compound. Propylene oxide, $CH_3\overset{\frown{O}}{CHCH_2}$ was identified[15] as propylene glycol. The slow oxidation of propylene is very similar to the oxidation of ethylene, proceeding through the formation of the olefin oxide and of acids and aldehydes containing the same and fewer numbers of carbon atoms as the original hydrocarbon.

Homogeneous Nature of the Ethylene Oxidation.—A Pyrex tube 2.5 cm. in diameter by 30 cm. long packed with 4-mesh broken Pyrex glass was heated in a tube furnace. The volume of the free space was 57.5 cc. A capillary exit tube of 2 mm. bore was sealed to the bottom of the vertical reaction vessel, and the capillary was sealed to a spiral trap. The exit capillary and receiver were cooled in an ice-bath so that less than an inch of the capillary was heated above the temperature of the bath. A mixture of 80% ethylene–20% oxygen was passed through the vessel at 450° with a time of contact of seventy seconds. No reaction between oxygen and ethylene was observed. The packed vessel was then fused to a one-liter reaction vessel (see above), which was heated in a tube furnace. The connecting tube between the vessels was 2.5 cm. long by 1.6 cm. in diameter. The narrow space between the furnaces was packed with asbestos. The gas mixture was passed from the packed tube at 450° directly into the empty vessel, which was heated to 315° with a time of contact in the empty tube of twenty-seven seconds. Reaction took place in the connecting tube and in the empty vessel, giving the following yield of liquid products based on the ethylene oxidized: ethylene oxide 11.6%, formaldehyde 34.7%, formic acid 6.9%. This striking experiment showed that in packed vessels where the free space is 1 to 2 mm. in diameter, the initiation and propagation of reaction chains was entirely suppressed even at temperatures over 100° above the temperature at which rapid reaction took place in a vessel where the free space was of the order of 50 mm. In this experiment the homogeneous nature of the reaction was demonstrated although the data in Table V and Table VI show that an important step in the reaction is conditioned by the surface of the vessel. The writer is aware of the contradiction in these results. These data indicate that the reaction chains are initiated, continued and terminated by the surface. The experiments using Pyrex, potassium chloride-coated Pyrex and fused silica vessels in which a variation in the composition of the reaction products was observed, but where the total amount of ethylene oxidized was the same, point to the fact that the reaction

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[15] Denigès, *Ann. chim.*, [8] **18**, 174 (1909).

chains are initiated and continued by the surface.   The chains may start at the surface and spread out in the gas phase, but the nature of the surface determines the products of the reaction.   The experiments with a potassium silicate-coated Pyrex vessel and steel and aluminum vessels, in which only half as much ethylene was consumed as in the other vessels, show that the surface can terminate chains or inhibit their formation altogether even in large vessels, as well as influence the nature of the reaction which does take place.   It cannot be decided from these experiments what the nature of the surface action is, that is, whether the action of the surface is a general property or is centered in specific portions of the surface, some of which catalyze reaction and chain propagation and some of which are inert or act to prevent reaction, but it is evident that the reaction is mainly homogeneous and of the chain type and that at least one step in the primary oxidation process takes place at a surface.

Discussion

Comparison of the rates of oxidation of ethylene in packed and unpacked vessels shows that the reaction is mainly a homogeneous gas reaction, for increasing the glass surface does not increase the rate but brings about a great decrease in the reaction velocity; in fact, the reaction is entirely inhibited in a packed vessel up to temperatures of 450°.   This phenomenon has been shown[16] to be characteristic of reactions which follow a chain mechanism.   The fact that the temperature range of the slow oxidation is lowered markedly on increasing the size of the reaction vessel, as shown by a comparison of the data in Table I with a 65-cc. vessel at 360–410° and in Table V using a one-liter vessel at 350–365°, is further evidence of the predominantly homogeneous nature of the reaction.   The change in the products of reaction in vessels of the same size made of different materials indicates that, although the reaction is mainly homogeneous, the surface plays an important role in the course of the reaction.   Further work along the lines of beam experiments and experimentation with vessels of different dimensions would be fruitful in throwing light on the influence of surface in this reaction.

The dependence of the reaction velocity on a high power of the ethylene concentration and its practical independence of oxygen, which is an essential reactant, suggest[1f] that the reaction chains are propagated through collision of a primary reaction product with ethylene.   Similar observations in the oxidation of acetylene,[17] of benzene,[18] of higher saturated hydrocarbons[19] and of hydrogen,[20] indicate that the kinetics of these reactions may be dependent on processes common to all of them.

A careful examination of the products of the reaction has shown that several carbon compounds are found in the slow combustion of ethylene

    [16] Semenoff, *Z. Physik*, **46**, 109 (1927); Pease and Chesbro, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928).

    [17] Kistiakowsky and Lenher, *Nature*, **124**, 761 (1929).

    [18] Fort and Hinshelwood, *Proc. Roy. Soc.* (London), **A127**, 318 (1930).

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

    [20] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **A122**, 610 (1929).

which have not been found in this reaction before; these products are ethylene oxide, dioxymethyl peroxide and glyoxal. The absence of dioxymethyl peroxide in the small-scale experiments at long times of contact, and the absence of glyoxal in the larger-scale runs indicate that these compounds are probably formed in secondary reactions, while the occurrence of ethylene oxide in considerable amounts in both series of experiments and its stability toward oxygen show that the formation of ethylene oxide is a principal primary reaction.

Controlled chemical tests have shown that hydrogen peroxide occurs in the slow reaction between oxygen and ethylene, and that its formation precedes that of the only other peroxide found, dioxymethyl peroxide. The occurrence of hydrogen peroxide and of organic peroxides in auto-oxidations and the slow combustion of the hydrocarbons has been a point of controversy for many years.

Lwow[21] and Kingzett[22] showed in the auto-oxidation of turpentine and essential oils the presence of a substance giving a blue color with chromic acid–ether, which was assumed to be hydrogen peroxide. However, Engler and Weissenberg[23] attributed this test to a secondary reaction of a peroxide of the oil (turpentine) with water, forming hydrogen peroxide. Then Clover and Richmond[24] in a study of the hydrolysis of organic peroxides and peracids showed that hydrogen peroxide was a product of the action of water on aliphatic and aromatic peroxides and peracids but that the reaction was a slow one, some hours being required to get a test for hydrogen peroxide from the hydrolysis. They concluded that, "None of·the peroxides which we have examined respond to this test (blue color with chromic acid–ether, or brown color with titanium sulfate) except on standing." The present work is in agreement with this statement of Clover and Richmond. Hydrogen peroxide and metallic peroxides, as calcium, zinc and barium peroxide, which give hydrogen peroxide with water, gave the tests instantly, while benzoyl peroxide, dimyristoyl peroxide, dipalmityl peroxide, dioleyl peroxide, and others in aqueous solution or in acetone–water solution did not give a test for hydrogen peroxide on standing for several hours. As the products of ethylene oxidation gave an instantaneous strong test for hydrogen peroxide, it was concluded that however hydrogen peroxide was formed in the reaction it was not a product of a hydrolysis in the test itself.

Discussion of the mechanism of the reaction and a theory of the formation of the various products will be presented in Part II of this paper after additional data on the course of the reaction have been considered.

[21] Lwow, *Z. Chem.*, [2] **6**, 626 (1870).

[22] Kingzett, *J. Chem. Soc.*, **27**, 511 (1870).

[23] Engler and Weissenberg, *Ber.*, **31**, 3046 (1898).

[24] Clover and Richmond, *Am. Chem. J.*, **29**, 179 (1903).

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Summary

The slow thermal oxidation of ethylene was studied in small Pyrex vessels and in one-liter vessels of glass, silica, potassium silicate-coated Pyrex, potassium chloride-coated Pyrex, steel and aluminum. The products of reaction under these conditions were formaldehyde, ethylene oxide, formic acid, the oxides of carbon and water. In addition, glyoxal occurred in the experiments in small vessels, and dioxymethyl peroxide was a principal product of the larger-scale runs.

Evidence of the formation of hydrogen peroxide in the oxidation of ethylene was given.

Comparison of the rates of reaction in packed and unpacked vessels showed that the reaction is mainly homogeneous and of the chain type. Change in the rate of reaction and in the amounts of the various reaction products on changing the surface of the reaction vessel indicated that some steps in the reaction took place at the wall of the vessel.

The velocity of reaction is dependent on the third power of the ethylene concentration and is practically independent of oxygen.

Packing the reaction vessel prevents reaction below 450°; above this temperature a heterogeneous oxidation to the oxides of carbon and water takes place.

The presence of nitrogen oxides does not catalyze the homogeneous reaction between oxygen and ethylene.

The reaction between oxygen and propylene at 300°, which yields a complexity of products, appears to follow the same mechanism as the oxidation of ethylene.

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