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THE REACTION BETWEEN OXYGEN AND ETHYLENE. II

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The first part¹ of this paper described an investigation of the kinetics of the slow combustion of ethylene in which the products of the reaction at relatively low temperatures and long times of contact were determined. The second part of the paper gives a quantitative study of the reaction at temperatures above 410° and with short times of contact. On the basis of these data a theory will be outlined which accounts for the observed products and for the abnormal kinetics.

Experimental

Re-circulation Experiments.—The reaction was studied at short times of contact in the re-circulation apparatus shown in Fig. 1. The gas mixture was stored in a sheet-iron, bell-type gas-holder of 57 liters capacity. The sealing fluid was a 1 glycerol : 1 water mixture in which ethylene and oxygen,² and carbon monoxide are practically insoluble. The volume of the bell was calculated from its dimensions. Indication of a pointer on the top of the bell on a fixed millimeter scale showed the volume of gas in the holder, and in the whole system. Ten millimeter iron pipe connected the gas-holder with the pump and the charcoal tube through 13-mm. gate valves. All other connecting pipes were of 16 mm. Pyrex glass tubing. The gas was circulated by a small rotary pump (a No. 1401 Cenco Blower, Central Scientific Co.) fitted with a gas-tight packing gland. The pump was run at constant speed by an a. c. motor. Flow of gas was regulated by a cock in a by-pass around the pump. The moving parts of the pump were lubricated with a few drops of oil. A trap of cotton waste removed any oil spray from gas leaving the pump. This pump was found to operate satisfactorily when the pressure in the system was within two inches of mercury of atmospheric pressure. The rate of flow of gas was measured with a Rotameter (Rotaworks, Aix-la-Chapelle), which was calibrated against a wet test meter over a flow from 5 cc./sec. to 200 cc./sec. The metered gas mixture was passed through the pre-

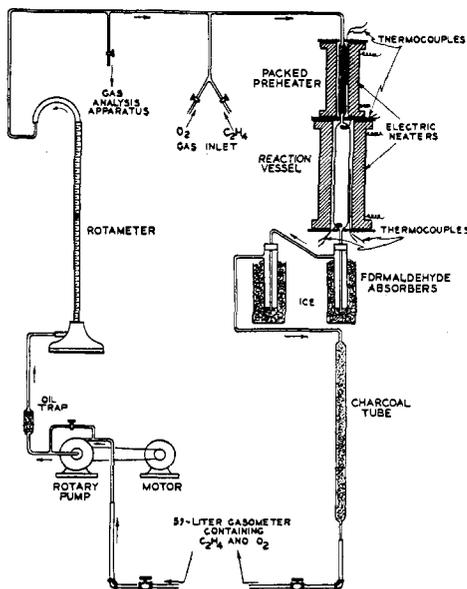


Fig. 1.—Re-circulation apparatus.

mercury of atmospheric pressure. The rate of flow of gas was measured with a Rotameter (Rotaworks, Aix-la-Chapelle), which was calibrated against a wet test meter over a flow from 5 cc./sec. to 200 cc./sec. The metered gas mixture was passed through the pre-

¹ Lenher, *THIS JOURNAL*, 53, 3737 (1931).

² Blair and T. S. Wheeler, *J. Soc. Chem. Ind.*, 41, 304T (1922).

heater packed with 4-mesh broken Pyrex glass and a 960-cc. reaction vessel shown in Fig. 1. After reaction the gases passed through two large wash-bottles, cooled with ice, with 2.5-cm. head of water in each, to absorb formaldehyde and formic acid, and then through a 5-cm. tube 75 cm. long filled with absorbent charcoal where ethylene oxide, hydrocarbons formed in the reaction, and the last traces of formaldehyde were recovered. The gases from the charcoal tube were returned to the gas-holder. Side tubes between the flowmeter and the preheater served in filling the apparatus and for taking samples for gas analyses.

In an experiment 75 cc. of water was placed in each of the ice-cooled wash bottles, the charcoal tube was packed with 300 g. of active charcoal, and all connections were made gas-tight. Ethylene was passed into the system, saturating the charcoal and the water in the wash-bottles and sweeping out air. The gas-holder was partly filled and the system pumped out a number of times to remove air. The system was then filled with an ethylene-oxygen mixture; the oxygen was added to ethylene in the system while the gas was circulating to effect thorough mixing. Analysis of the gas mixture established the composition of the gas mixture and the volume of each constituent as the volume of the system was known. The furnaces were heated to the temperature of experiment while gas was circulated. Since the runs were carried out with a high hydrocarbon concentration and a low oxygen concentration (80-90% C_2H_4 and 10-20% O_2) and the gases were consumed in approximately the ratio $1C_2H_4 : 1O_2$, oxygen was supplied during the run at its rate of consumption. The inflow of oxygen was metered with a capillary flowmeter and a wet test meter to give both the rate of addition and the total amount added. Heating of the reaction vessel was controlled by an Engelhardt temperature controller, and the temperature of the walls was read from a thermocouple in a glass tube placed against the wall in the middle of the furnace. The temperature of the reacting gases, which was taken as the reaction temperature, was measured on a thermocouple in a 4-mm. tube which projected into the middle of the vessel at the entrance from the preheater. The junction of this thermocouple was at the tip of the 4-mm. tube. The temperature of the gas leaving the reaction vessel was read on a thermocouple placed in the outlet of the vessel in a position similar to that of the one in the entrance.

Analyses of the solutions in the wash-bottles for formic acid (both as free acid and as acid from dioxymethyl peroxide) and for total aldehyde as formaldehyde were carried out as described in Part I.³ Formaldehyde was determined by the silver cyanide method⁴ and when acetaldehyde had been found qualitatively to be present, the difference between the formaldehyde and the total aldehyde (calculated as formaldehyde), determined by the bisulfite method, was calculated as acetaldehyde. Only traces of glycol, coming from small amounts of ethylene oxide dissolved in the acid solution, were detected and analysis was not possible. The solution of ethylene oxide in the wash-bottles was small due to the presence of low concentrations of about 0.1% ethylene oxide in the fast-moving hot gas stream from the furnaces. The ethylene oxide and higher unsaturated hydrocarbons and traces of formaldehyde were absorbed by the charcoal and were recovered from it by steaming. The charcoal containing the products from a run was placed in a flask, heated slowly to 130° and steamed. The gases and steam were cooled with a 75-cm. condenser, and water, ethylene oxide, and traces of formaldehyde were collected in a water-bubbler cooled in ice. The last traces of ethylene oxide and the higher hydrocarbons (when present) were recovered

³ Lenher, Ref. 1, p. 3744.

⁴ Cumming, "Systematic Organic Chemistry," D. Van Nostrand Co., New York, 1924, p. 479.

in a long spiral trap cooled with solid carbon dioxide-methanol mixture. The ethylene oxide solutions were analyzed as described in Part I.⁵

When higher unsaturated hydrocarbons were formed in the reaction, the analysis of the fraction boiling below room temperature was carried out in a Podbielniak⁶ fractional-distillation apparatus. The hydrocarbons boiling above room temperature were determined from their boiling range and by chemical tests.

Experiments carried out with the re-circulation apparatus are summarized in Table I. The average duration of the experiments in Table I was four hours.

TABLE I
REACTION BETWEEN OXYGEN AND ETHYLENE IN RE-CIRCULATION APPARATUS
USING PACKED PREHEATER AND 1-LITER REACTION VESSEL OF PYREX GLASS

Experiment	Temperature, °C.		Time of contact, sec.	Init. composition of gas, %		Ethylene consumed, g.
	Reaction vessel	Preheater		C ₂ H ₄	O ₂	
53	410-15	430	3.1	71.0	13.0	16.39
54	435	460	3.0	80.4	9.9	27.29
55	505	505	3.0	87.0	8.8	37.34
56	410-30	540	2.9-16.0	10.0	10.7	...
57	485	525	3.0	85.9	8.5	47.51
3a	535	515	2.7	95.0	No O ₂ used	...
6a	490	510	3.0	98.3	1.0 cc.	18.73
					per sec. fed during run	
8a	600	460	2.5	94.3	0.5 cc.	24.10
					per sec. fed during run	

Experiment	Yield of products in per cent. based on ethylene consumed					
		Total aldehyde	HCOOH	CO + H ₂	CO ₂	Higher olefins
53	21.00	65.70	3.20	10.10
54	21.27	60.63 ^a	1.22	12.31	1.35	...
55	17.57	18.70 ^b	2.92	27.40	2.90	30.50
56
57	14.44	38.90 ^c	4.06	19.20	4.44	18.94
3a
6a	11.23	11.95 ^d	0.44	7.30	0.50	53.60
8a	2.90	13.73 ^e	.16	6.64	.70	74.25

^a Acetaldehyde, 13.53%; formaldehyde, 47.10%. ^b Acetaldehyde, 0.70% doubtful analysis; formaldehyde, 18.00%. ^c Acetaldehyde, 17.80%; formaldehyde, 21.10%. ^d Acetaldehyde, 2.15%; formaldehyde, 9.80%. ^e Acetaldehyde, 4.15%; formaldehyde, 9.58%.

The complexity of the reaction between oxygen and ethylene is the most striking feature of the experiments in Table I. It is evident from

⁵ Lenher, Ref. 1, p. 3744.

⁶ The Podbielniak apparatus, *Ind. Eng. Chem., Anal. Ed.*, 3, 177 (1931), is essentially an all-glass still with a vacuum-jacketed column cooled with liquid air, and an evacuated receiver. The writer wishes to acknowledge his indebtedness to Dr. D. F. Babcock for the hydrocarbon distillations in the Podbielniak apparatus.

these data and the experiments in Part I that the course of the reaction and the nature of the reaction products depend entirely on the conditions under which the reaction is carried out, and that any general scheme of a mechanism of the reaction must permit a wide variation in the importance of the reactions involved. In these recirculation experiments two products occur, acetaldehyde and higher olefins, which play no part in the reaction at lower temperatures or with different concentrations of reactants.

Experiments 53, 54, 55 and 57 were carried out with the oxygen concentration maintained at about 10%; as ethylene and oxygen were consumed during a run, oxygen was fed in at a rate which was controlled by rapid analysis using a modified Haldane apparatus. In Experiment 53, 90% of the ethylene consumed was recovered as liquid products, and there was no reason to believe that with times of contact shorter than three seconds, the conversion to liquid products would not be quantitative. This is direct evidence that the whole course of the slow combustion takes place in a series of steps, the formation of partially oxidized products preceding the appearance of carbon oxides and steam, as has been suggested by Bone and R. V. Wheeler, and Blair and T. S. Wheeler. Acetaldehyde appeared as a product above 415° (Experiment 54) and was formed in considerable amounts at 485° (Experiment 57). The acetaldehyde analysis in Experiment 55 is probably incorrect owing to the interference of dioxymethyl peroxide in the precipitation of silver cyanide in the determination of formaldehyde. It appears from these data that acetaldehyde is formed either in a primary reaction of oxygen and ethylene, or that it comes from the rearrangement of ethylene oxide which is formed in increasing yields at the expense of formaldehyde. The yields of ethylene oxide increase with temperature up to 435° (compare data in Table VI, Part I, with Experiments 53 and 54, Table I above) and above this temperature the yields of both formaldehyde and ethylene oxide fall off with increase of temperature. Ethylene oxide is thermally stable up to 400°, but above 440° it rearranges rapidly in a monomolecular reaction to acetaldehyde.⁷ The appearance of acetaldehyde in considerable amounts at 435° is thus in qualitative agreement with its formation by the rearrangement of ethylene oxide. However, at 435° the observed yield of ethylene oxide remains around the 21% which is found at a slightly lower temperature when acetaldehyde does not occur; and at the same time the yield of formaldehyde has fallen from 65% at 415° to 47% at 435° with only a 3% increase in the products other than acetaldehyde. The decrease in the amount of formaldehyde (18%) is thus sufficient to account for the formation of acetaldehyde (13%) from ethylene oxide, which in turn had been formed at the expense of formaldehyde in a competitive primary

⁷ Heckert and Mack, *THIS JOURNAL*, 51, 2706 (1929).

reaction. While the origin of acetaldehyde is not established by these experiments, the data are entirely compatible with the assumption that it is formed from a thermal rearrangement of ethylene oxide. The formation of acetaldehyde from ethylene oxide by a simple unimolecular process is much more probable than its formation from ethylene and oxygen, involving the breaking of the strong bond between the two atoms in an oxygen molecule.

Carbon monoxide was the principal gaseous product in all experiments below 480° , which indicated that the decomposition of formic acid and of dioxymethyl peroxide was the main source of the end products of reaction. As the ratio of carbon monoxide:hydrogen was always about 5:1, it is probable that both reactions occurred. Carbon dioxide was formed from oxidation and decomposition of formaldehyde and formic acid, and only in the higher temperature experiments is it probable that its occurrence was due to oxidation of carbon monoxide.

The effect of the concentration of the reactants on the rate of reaction is shown in Experiment 56, in which no measurable reaction was observed in a 10% oxygen: 10% ethylene mixture diluted with nitrogen and carbon monoxide, even at a time of contact of sixteen seconds at 430° .

The amounts of ethylene oxidized given in Table I were calculated from the ethylene content of the products found by analysis. These figures were checked by the volume of gas which disappeared during the reaction, as calculated from the initial and final composition of the gas and the observed volume change in the system. In spite of the absorbent charcoal in the system saturated with a large volume of ethylene, from which ethylene was displaced to a certain extent by the ethylene oxide and higher olefins formed in the reaction, the ethylene consumption calculated from the products agreed within 10% with the ethylene consumption calculated from the gas analyses and the gas-holder readings.

Discussion

Activation and Polymerization of Ethylene.—In experiments above 450° the formation of higher olefin hydrocarbons was noted. These hydrocarbons were absorbed on the charcoal in the recovery system and were recovered as liquids at -80° on steaming out the charcoal. Analysis of the liquid hydrocarbons in the Podbielniak still showed them to be mainly propylene with smaller amounts of butylene. A number of experiments with high ethylene concentrations and oxygen concentrations of about 5% during a run showed that below 520° (450 – 520°) propylene and butylene were the only hydrocarbons formed. There was no oil or tar formation observed, and the gas analyses gave no evidence of the formation of saturated hydrocarbons greater than 0.5% of the ethylene consumed. In Experiment 55 the 30.50% yield of higher olefins proved on distillation

to be 83% propylene (b. p. -47°) and 14.6% butylene (b. p. -6°). An experiment at 460° similar to Experiment 55, in which some of the propylene was lost during distillation, showed the composition of the higher olefins distilled to be 66.9% propylene and 21.5% butylene. This unexpected discovery of propylene as the principal polymerization product of ethylene was further investigated in a series of experiments (3a, 6a and 8a are given in Table I) using ethylene and less than 1% of oxygen during a run. Oxygen-free ethylene was not polymerized at 535° at a time of contact of 2.7 seconds, as shown in run 3a. At 490° with 98% ethylene at the start of the run (80.60% at the end) and 0.5–0.7% oxygen (the oxygen was fed in at a rate of 1 cc./sec. and was entirely consumed) 53.60% of the ethylene reacted was polymerized and 46.4% was oxidized. The polymerized product was 91.4% propylene and 8.6% butylene. In Experiment 8a at 600° with 94% ethylene at the start of the run (67.1% at the end) and 0.4% oxygen during the run in a silica apparatus (preheater and reaction vessel), three times as much ethylene was polymerized as was oxidized. The hydrocarbon product was 59.3% propylene (10.42 g.) and 12.2% butylene (2.15 g.) (determined by distillation in the Podbielniak still), and 28.4% amylenes (5.00 g.) boiling from $32-40^{\circ}$. The fraction which was assumed to be amylenes was insoluble in water, absorbed bromine, decolorized potassium permanganate, had the characteristic "olefin" smell and boiled over the range $32-40^{\circ}$, at which the amylenes boil. This run at 600° was the only one in which the formation of saturated hydrocarbons was observed; in this experiment (8a) 1.66% of the ethylene consumed yielded methane.

These experiments at high temperatures and short times of contact with high ethylene concentrations throw new light on the chemistry of ethylene. Perhaps the most interesting feature of these experiments is the formation of propylene from ethylene. It is evident that oxygen activates ethylene to react with itself as well as to react with oxygen, for when no oxygen is used, other conditions remaining the same, no change is observed in ethylene. Further, this polymerization activated by oxygen is a much faster reaction than the thermal polymerization of pure ethylene: in the present experiments 1 to 5% of the ethylene reacted during a time of contact of three seconds between 480 and 600° , while with pure ethylene⁸ at 500° 8% reacted during a time of contact of 380 seconds, and at 600° 34% reacted in 340 seconds. The thermal polymerization of ethylene has long been known to proceed through the formation of higher mono-olefins.^{8,9} It has been assumed¹⁰ recently that butylene was the primary

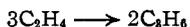
⁸ Pease, *THIS JOURNAL*, **52**, 1158 (1930).

⁹ (a) Day, *Am. Chem. J.*, **8**, 153 (1886); (b) Bone and Coward, *J. Chem. Soc.*, **93**, 1197 (1908).

¹⁰ (a) Hague and Wheeler, *J. Chem. Soc.*, 391 (1929); (b) Wheeler and Wood, *ibid.*, 1819 (1930); (c) Pease, *THIS JOURNAL*, **53**, 613 (1931).

product of the reaction. The basis for this assumption appears to be an experiment of Wheeler and Wood^{10b} with ethylene at 650° in which 8.4% of the ethylene passed was recovered as gases containing four carbon atoms, and the work of Mignonac and de Saint-Aunay¹¹ on the formation of butylene from ethylene in the electric discharge. Pease,^{8,10c} while assuming that the ethylene polymerization takes place with the primary formation of butylene in an association reaction, has found that the energy of activation of the reaction and the temperature coefficient are not in agreement with the rate of a bimolecular reaction, $2C_2H_4 \longrightarrow C_4H_8$, calculated on the collision theory of reaction, and he points out the kinetic difficulties which this assumption presents. Frey and Smith¹² in studying the decomposition of ethylene in silica vessels with a time of contact of four minutes at 575° observed the formation of relatively large amounts of propylene (4.5% propylene as compared to 1.2% butylene in the reacted gas), and in the decomposition of propylene under the same conditions they found that the principal product of polymerization was butylene, with large amounts of methane and ethylene. These experiments of Frey and Smith show that in the polymerization of ethylene, even in the absence of oxygen, propylene is the olefin which is found in the largest quantities. Wheeler and Wood^{10b} observed in the thermal decomposition of the Δ^{α} and Δ^{β} butylenes at 600° that the formation of propylene was accompanied by the occurrence of an equal volume of methane. The butylenes are quite stable at the temperatures of 450–600° and the short times of contact used in the present experiments. Moreover, in the experiments in Table I the formation of methane was observed in only a single run, and in that instance only to the extent of 1.6% of the ethylene reacted. Thus the propylene formed in these experiments could not have been formed from the decomposition of butylene initially produced into propylene and methane. Propylene is the principal primary product of the polymerization of ethylene activated by oxygen, and it is reasonable to conclude that propylene is a primary product of the thermal polymerization of pure ethylene.

The formation of propylene from ethylene can be interpreted in several ways: first, consider the formation of two molecules of propylene in a termolecular collision of three ethylene molecules.



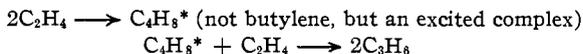
This reaction is a possible one, but the frequency of termolecular collisions at high temperatures is so small¹³ that the rate of formation of propylene from ethylene does not appear to be accounted for by a third-order reaction.

¹¹ Mignonac and de Saint-Aunay, *Compt. rend.*, 189, 106 (1929).

¹² Frey and Smith, *Ind. Eng. Chem.*, 20, 950 (1928).

¹³ Bodenstein, *Z. physik. Chem.*, 100, 68 (1922); Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, 2d ed., 1929, p. 119.

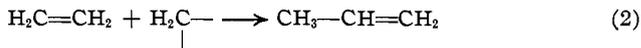
Second, there is the possibility of the formation of propylene in a sequence of bimolecular reactions involving excited intermediate molecules, which is given by the equations



These reactions are kinetically possible, but in the lack of experimental evidence for the existence of the C_4H_8^* molecule, which at best must be extremely short-lived, it is problematical to assume its formation in an association reaction, as Pease has pointed out.^{10c} The simplest explanation of the formation of propylene from ethylene is found in the assumption of the existence of methylene radicals which are formed from the dissociation of ethylene



and the reaction of these methylene groups with ethylene to form propylene

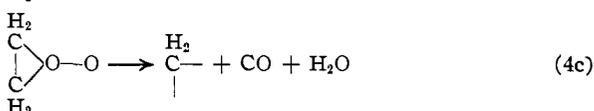
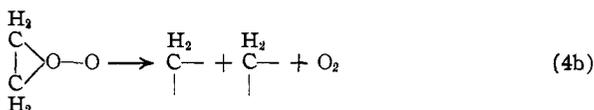
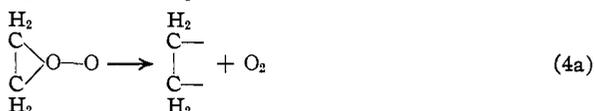
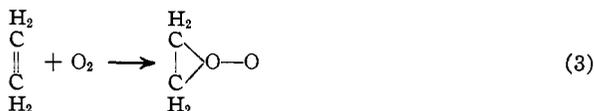


If the presence of methylene groups is assumed, the formation of large amounts of propylene from ethylene in this reaction is simple to interpret, for the chemical unsaturation of methylene radicals can be satisfied by reaction with the large excess of ethylene to form propylene directly. This reaction (2) is thermochemically possible, for the formation of propylene from ethylene is an exothermic reaction, proceeding with a decrease in free energy.

The assumption of methylene groups in the reaction, which is strongly supported by chemical evidence, makes it necessary to account for their formation. Methylene radicals are formed by the scission of the $\text{C}=\text{C}$ bonds in ethylene with which an energy of approximately 125 k.-cal./mole is associated.¹⁴ The value of the $\text{C}-\text{H}$ linkage in olefins is 92 k.-cal./mole and that of the $\text{C}-\text{C}$ bond is 71 k.-cal./mole. These figures indicate that unless there is an activation of the $\text{C}=\text{C}$ to lower the energy of dissociation below that of the $\text{C}-\text{H}$ bond, one would expect a dehydrogenation of ethylene to acetylene before a breaking of the carbon double bond. Experiments 6a and 8a of Table I give direct experimental evidence of the activation of ethylene by oxygen, for in these experiments not only is ethylene brought to reaction with itself by oxygen but actually *more* ethylene reacts with itself than is oxidized. It has already been pointed

¹⁴ This speculation on the formation of methylene radicals is given merely to point out some of the difficulties in attempting to justify the assumption of their existence. The figures for the energies associated with specific linkages are very uncertain and are used here with reservations; the actual figures are those of Grimm and Wolf, "Geiger-Scheel, Handbuch der Physik," Julius Springer, Berlin, 1927, Vol. XXIV, p. 536, based on the calculations of Fajans, *Ber.*, 53, 643 (1920), and von Weinberg, *ibid.*, 53, 1347 (1920).

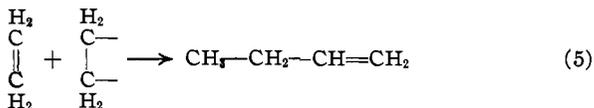
out above (page 3757) that the rate of polymerization of ethylene is greatly increased by the presence of oxygen. To explain this activation of ethylene by oxygen without actual oxidation or dehydrogenation, it is reasonable to assume that the C=C bond is activated or opened up by oxygen in some such manner as this



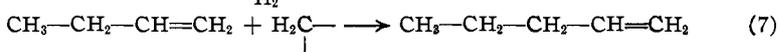
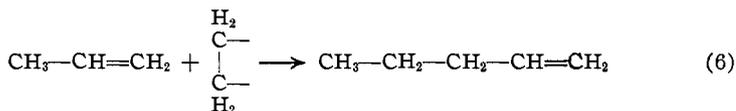
Equation 3 represents the addition of molecular oxygen at the olefin double bond in which one of the carbon-carbon bonds is opened up. The breaking of this carbon-carbon bond may be assumed to absorb sufficient energy from the reactant molecules to lend a transient existence to the resultant molecule, $\begin{array}{c} \text{H}_2\text{C} \\ | \\ \text{C} \\ | \quad \diagdown \\ \text{C} \quad \diagup \quad \text{O}-\text{O} \\ | \\ \text{H}_2\text{C} \end{array}$. The formation of an active ethylene molecule on dissociation of the addition compound with oxygen is represented by Equation 4a.

Methylene radicals are formed by Reaction 4b, in which the carbon-carbon bond in the addition complex is broken on decomposition, yielding two methylene radicals and oxygen. In Reaction 4c one methylene radical is formed if in the decomposition the oxygen in the complex reacts with one of the residues.

The high ratio of propylene to butylene observed in the polymerization products of ethylene in the high temperature experiments shows that the dissociation of ethylene into methylene radicals is the more important activation process. Butylene is presumably the product of a reaction of the type



and the amylenes which are formed at 600° in these experiments (8a, Table I) may be formed in such reactions as



If the energy of activation of Reaction 3 is greater than 37 k.-cal./mole and the energy of dissociation of the C=C bond is lowered by this amount, the formation of methylene groups from ethylene becomes possible, for the dissociation energy of the C=C bonds is now less than the 92 k.-cal. required to break the C-H bond.¹⁵ An energy of activation of 37 k.-cal./mole for a thermal process depending on the breaking of a homopolar valence binding at a measurable rate at temperatures of 500° appears to be a possible one.¹⁶ All the evidence of these experiments points to the formation of an active modification of ethylene, as $\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ | \quad | \end{array}$ and of methylene radicals, $\begin{array}{c} \text{H}_2\text{C}- \\ | \end{array}$, on activation of ethylene by oxygen. The structure of the ethylene molecule, as discussed by Lewis¹⁷ and by Carothers,¹⁸ in which the repulsion of the carbon nuclei makes dissociation into radicals and the existence of active forms possible, is in agreement with the present considerations. The dependence of the rates of combustion and of polymerization of ethylene on a high power of the ethylene concentration observed here suggests that these reactions proceed through an activation of ethylene. The similar influence of high hydrocarbon concentration in the oxidation of acetylene¹⁹ indicates that in this reaction also, and in the combustion²⁰ and polymerization of the aliphatic unsaturated hydrocarbons generally, the process may proceed through an activation of the hydrocarbon.

General Outline of the Oxidation of Ethylene.—The experiments described above carried out under a wide variety of conditions of temperature, gas composition, and time of contact in vessels of different sizes and made of different materials reveal the astonishing complexity of the slow combustion of ethylene. The various reactions and phenomena

¹⁵ The activation energy required in Reaction 3 may be very much less than 37 k.-cal. to make the energy of separation of the C=C bond less than that of the C-H linkage, for if the energy of separation of C=C is as low as 111 k.-cal./mole (the value of 125 k.-cal./mole used above is one of the more unfavorable cases, see Grimm and Wolf¹⁴), an activation energy of only 20 k.-cal./mole is necessary to make possible the formation of methylene radicals. The different values in the literature for the heat of combustion of ethylene make the value of C=C in ethylene uncertain at present.

¹⁶ Von Hartel and Polanyi, *Z. physik. Chem.*, **11B**, 97 (1930).

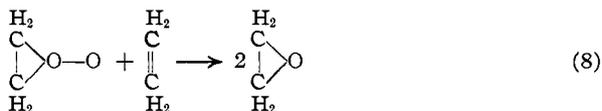
¹⁷ (a) Lewis, *THIS JOURNAL*, **38**, 762 (1916); (b) Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, 1923, p. 124.

¹⁸ Carothers, *THIS JOURNAL*, **46**, 2226 (1924).

¹⁹ Kistiakowsky and Lenher, *ibid.*, **52**, 3785 (1930).

²⁰ Compare Bodenstein, *Z. physik. Chem.*, **B12**, 151 (1931).

water can take place in a direct reaction between ethylene and oxygen, for it was shown that at short times of contact ethylene can be oxidized quantitatively to intermediate products. The early occurrence of carbon oxides and water can be accounted for by oxidation of formaldehyde, or by reaction of the addition complex with oxygen. Evidence for the activation of ethylene through the formation of an addition complex (or "mol oxide," or peroxide, as these compounds may be called) has been given in the preceding section. Engler and Wild²² and Bach²³ found evidence for the formation of addition complexes or peroxides in the oxidation of compounds containing double bonds by oxygen; and, more recently, Callendar²⁴ and Egerton and Gates²⁵ have suggested that the initial process in a hydrocarbon combustion is the formation of a peroxide. Ethylene oxide is formed from the addition compound in a collision with ethylene, and in a collision with a water molecule. The formation of ethylene oxide in the reaction



helps to explain the dependence of rate of reaction on high ethylene concentrations, and is in agreement with the assumption of Hinshelwood that the reaction chains are short,²⁶ for only two ethylene molecules can be brought to reaction in one primary process in this reaction. Further, the assumption of Reaction 8 accounts for the formation of ethylene oxide, containing one oxygen atom, directly from ethylene, and avoids the difficulties involved in assuming a dissociation of oxygen into atoms or the formation of hypothetical compounds, as vinyl alcohol,²⁷ containing one oxygen atom.

The reaction between the addition complex, or peroxide, and water to form ethylene oxide and hydrogen peroxide is in accordance with the behavior of organic peroxides.²⁸ The formation of hydrogen peroxide has been observed by Pease²⁹ in the reaction of hydrogen with oxygen at 550°, and as this reaction displays kinetics which are abnormal and similar to the reaction between oxygen and ethylene, it may be that peroxide

²² Engler and Wild, *Ber.*, **30**, 1669 (1897).

²³ Bach, *Compt. rend.*, **124**, 2951 (1897).

²⁴ Callendar, *Engineering*, **123**, 147, 184, 210 (1927).

²⁵ Egerton and Gates, *J. Inst. Petroleum Tech.*, **13**, 281 (1927).

²⁶ Thompson and Hinshelwood, *Proc. Roy. Soc. (London)*, **A125**, 277 (1929).

²⁷ Bone and R. V. Wheeler, *J. Chem. Soc.*, **85**, 1637 (1904); Blair and T. S. Wheeler, *J. Soc. Chem. Ind.*, **41**, 310T (1922).

²⁸ See for example the work of Prileschajev, *Ber.*, **42**, 4811 (1909), on the formation of olefin oxides from the olefins and benzoyl peroxide in solution.

²⁹ Pease, *THIS JOURNAL*, **52**, 5106 (1930).

formation in these oxidations is associated with the unusual dependence of the reaction on the concentration of the reactants.³⁰ The occurrence of dioxymethyl peroxide and its probable formation from hydrogen peroxide and formaldehyde have been dealt with fully in Part I. It may be further noted that the marked effect of the walls of the vessel on the formation of dioxymethyl peroxide points to a catalytic action on the stability of a reactive substance like hydrogen peroxide. Experiments 26 and 27, Table VI, in Part I, with steam in the reactant gases, in which the yield of ethylene oxide is increased and the formation of the decomposition products of dioxymethyl peroxide is greatly increased, are in support of this reaction between hydrogen peroxide and formaldehyde as a step in the reaction sequence. The reaction of two molecules of formaldehyde and a molecule of hydrogen peroxide to form dioxymethyl peroxide may take place in two successive bimolecular reactions as suggested by Woker,³¹ rather than in a termolecular reaction. The other reactions given in this scheme have been discussed above.

The polymerization reactions proceed through the activation of ethylene in the reactions involving the ethylene-oxygen addition complex, or peroxide. It is quite possible that the whole reaction, including the formation of formaldehyde, may proceed through the primary formation of the oxygen-ethylene addition complex, but the occurrence of formaldehyde in large amounts in the early stages of the reaction and its presence in the reaction products under all conditions indicate that its formation is probably more direct than that of any other product.

These experiments show above all that the slow oxidation of the unsaturated hydrocarbons is a process of great complexity. The variety of products formed in the slow combustion of such a simple hydrocarbon as ethylene and the stability of some of the products, as the olefin oxides, show that the processes involved in these slow oxidations may be fundamentally different from the reactions taking place in explosive combustion. It is hardly to be expected that any theory of hydrocarbon combustion which is based on the phenomena of explosive combination can meet with more than a very limited application to the correlation and interpretation of the processes taking place in slow oxidations. The primary process which appears to be common in the slow oxidation of the unsaturated hydrocarbons is that of activation of the hydrocarbon, probably through the formation of an intermediate peroxide compound.

Summary

The slow reaction between oxygen and ethylene has been investigated in a re-circulation system at short times of contact between 410 and 600°.

³⁰ Thompson and Hinshelwood, *Proc. Roy. Soc. (London)*, **122A**, 610 (1929).

³¹ Woker, *Ber.*, **43**, 1024 (1914); Wieland and Wingler, *Ann.*, **431**, 301 (1923).

The principal reaction products are ethylene oxide and formaldehyde; other products whose formation depends on the conditions of experiment are dioxymethyl peroxide, acetaldehyde, formic acid, the oxides of carbon and water. At temperatures above 450° the polymerization of ethylene to higher mono-olefins becomes an important reaction. Propylene and small amounts of butylene are the primary polymerization products of ethylene.

The primary process in the reaction between oxygen and ethylene is the activation of ethylene, probably by the formation of an addition complex or peroxide. The reaction takes place in a stepwise sequence of consecutive reactions, ethylene oxide and formaldehyde are formed in the early stages of the oxidation preceding the appearance of acetaldehyde, dioxymethyl peroxide, formic acid, carbon oxides and water.

Hydrogen peroxide is formed in the reaction; dioxymethyl peroxide is probably formed from hydrogen peroxide and formaldehyde.

A scheme of the mechanism of the oxidation of ethylene has been outlined. Experiments on the oxidation of propylene have indicated that this mechanism of the oxidation applies to the slow combustion of the other members of the mono-olefin hydrocarbon series.

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TERNARY SYSTEMS: WATER, ISOPROPANOL AND SALTS AT 25°

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A search of the literature recently in connection with another investigation¹ revealed only one paper on the above systems.² Only two salts, potassium carbonate and potassium fluoride, were investigated in the systems with isopropanol. Some difficulties such as the precipitation of the salt by the addition of the alcohol and also the slow rate of separation of the two liquid phases seem to have deterred further work with other salts. It appeared desirable to extend the knowledge of the above systems in order to obtain some comparative data with other aliphatic alcohols and also on account of the increased commercial interest in recent years. This has been done by the authors qualitatively with about seventy-five common inorganic salts and quantitatively with ten of these salts. Qualitatively, it was found that out of these seventy-five inorganic salts chosen more or less at random two liquid phases were formed by more salts with isopropanol than with ethanol or methanol but with fewer salts if normal propanol and tertiary butanol were used for comparison. These five

¹ P. M. Ginnings and Dorothy Robbins, *THIS JOURNAL*, **52**, 2282 (1930).

² G. B. Frankforter and S. Temple, *ibid.*, **37**, 2697 (1915).