of the physical type, (b) *ad*sorption of the activated type and (c) a third process which is probably solution. The contribution of the individual processes to the total observed sorption has been estimated.

The distinguishing characteristics of each process have been further elucidated, particularly in respect to rates, equilibria, heats and thickness of adsorbed layers.

With all three gases at $-183°$ and below, the sorption consists solely of physical adsorption. In each case activated adsorption occurs at higher temperatures. The rate of this process is greatest for carbon monoxide and least for nitrogen. With hydrogen at 110° and above, the third process, ascribed to solution. comes into prominence.

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[CONTRIBUTION NO. 88 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO.]

THE REACTION BETWEEN OXYGEN AND PROPYLENE: ACTIVATION, OXIDATION AND POLYMERIZATION

BY SAMUEL LENHER

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It was recently shown in a study of the reaction between oxygen and ethylene[1] that activation of ethylene was a primary process in the reaction. This activation led to the formation of polymerization and pyrolysis products from ethylene, as well as oxidation products, under conditions where pure ethylene is not decomposed. The formation of the primary oxidation products, ethylene oxide and acetaldehyde containing one oxygen atom and the elements of ethylene in the molecule, and the formation of the polymerization products, propylene, butylenes and amylenes, without separation of hydrogen or direct formation of saturated hydrocarbons or carbon, showed that the activation of ethylene consisted in an activation of the double bond. Since the primary oxidation and decomposition reactions of ethylene could be interpreted adequately by assuming an activation of the double bond under the influence of heat or of oxygen, it seemed of value to determine whether the next member of the monoolefin series of hydrocarbons, propylene, behaved similarly. The work described in this paper leads to the conclusion that activation of the double bond in propylene is the primary process in the oxidation and polymerization reactions.

The oxidation of propylene has received little attention. In connection with the study of the oxidation of ethylene[2] some experiments on the oxidation of propylene at 280–315° showed that the liquid products of the

[1] Lenher, THIS JOURNAL, **53**, 2420, 3737, 3752 (1931).

[2] Lenher, Ref. 1, p. 3748.

reaction were propylene oxide, propionaldehyde, acetic acid, acetaldehyde, formic acid, formaldehyde and a peroxide compound, and that the mechanism of the slow oxidation was very similar to the oxidation of ethylene.

The thermal decomposition of propylene has recently been the subject of several investigations. However, a survey of these researches gives no clear picture of the principal primary reactions involved in the pyrolysis of propylene. Frey and Smith[3] concluded from a study of the decomposition of propylene at 575° and 760 mm. in a silica vessel with a time of contact of five minutes that the principal products of the polymerization of propylene (under these conditions) were butylene and higher hydrocarbons, as well as large amounts of methane and ethane. Their results show that the principal products were methane 10.4% ethylene 8.0%, propane 3.0%, butylene 2.8%, C_nH_{2n}(n = 5 to 8) 2.6% ethane 1.9% and hydrogen 1.7%. Wheeler and Wood[4] studied the decomposition of propylene at 650° in silica vessels at times of contact of twenty seconds and longer and reported the principal products to be ethylene, ethane, and butylene with small amounts of aromatic hydrocarbons. Recently Hurd and Meinert[5] reported on the pyrolysis of propylene in Pyrex glass and quartz at temperatures between 600 and 950° and times of contact of from half a second at 950° to thirty seconds and up to two minutes at the lower temperatures. They found that under their conditions propylene broke down to form simpler gases, the principal products being methane, ethylene, hydrogen, and paraffins higher than methane (principally ethane) in the ratio 3 : 3 : 1 : 1. The mechanism of the pyrolysis of propylene was considered to be the same as that suggested by Hurd and Spence[6] to explain the pyrolysis of isobutylene involving breaking of C—C and C—H bonds and a possible activation of the C=C bonds. Dunstan, Hague and Wheeler,[7] in a survey of the pyrolysis of the lower olefins, concluded that the principal primary reaction, common to all, was the formation of either two-carbon or four-carbon atom (or both) members of the mono-olefin series. They considered that the primary reaction in the pyrolysis of propylene was $2C_3H_6 = C_2H_4 + C_4H_8$.

Experimental

The reaction between propylene and oxygen, and the pyrolysis of oxygen-free propylene, were studied in the recirculation apparatus described in detail in a previous communication[8] using the same experimental procedure. A preheater and reaction vessel of fused silica were used in all the experiments. The only change in the apparatus was the use of a smaller charcoal absorption tube 24 mm. by 30 cm. containing 100 g. of

[3] Frey and Smith, *Ind. Eng. Chem.*, **20**, 950 (1928).

[4] Wheeler and Wood, *J. Chem. Soc.*, 1823 (1930).

[5] Hurd and Meinert, THIS JOURNAL, **52**, 4978 (1930).

[6] Hurd and Spence, *ibid.*, **51**, 3561 (1929).

[7] Dunstan, Hague and Wheeler, *J. Soc. Chem. Ind.*, **50**, 316T (1931).

[8] Lenher, Ref. 1, p. 3752.

charcoal, for the recovery of the higher olefins formed. The small amount of charcoal was used because the large volume of propylene absorbed by the charcoal made use of a larger amount impracticable to handle in a recovery system. The oxidation products were determined as outlined in the previous papers on ethylene oxidation.[9] Propylene was taken from commercial cylinders (Carbide and Carbon Chemicals Corporation). Fractional distillation showed it to be free from other olefins. Analysis showed the gas to be 98.0% propylene, 1.5% propane, 0.13% carbon dioxide and the remainder inerts, probably nitrogen.

Gas analyses were carried out in a Burrell gas analysis apparatus (Precision Type). The procedure of Hurd and Spence,[10] based on the differential absorption of the lower olefins in sulfuric acid of various concentrations, was used for the analysis of the unsaturated hydrocarbons (acetylene hydrocarbons absent). The directions given by Hurd and Spence were checked and found to be entirely satisfactory and dependable for the analysis of a mixture of ethylene, propylene and butylenes, or a complex mixture of these gases with carbon oxides, hydrogen and lower saturated hydrocarbons.

The higher olefins formed in the reaction and absorbed on the charcoal were recovered as liquids by heating the charcoal to 130–140° in a flask and steaming thoroughly. The gases and steam evolved were cooled with a long condenser and a water scrubber. The hydrocarbon products were recovered in a long spiral trap which was cooled in boiling liquid ammonia following the scrubber. As propylene boils at −47° and the temperature of boiling liquid ammonia is −38.5° the excess of propylene from the absorbent charcoal was not condensed with the products. The identity of the hydrocarbon products was established by fractional distillation, giving the boiling point of each constituent, and by chemical tests and analyses. The hydrocarbons boiling below propylene, which were not absorbed by the charcoal saturated with propylene, were allowed to build up together with carbon oxides in the recirculation system, and were determined by gas analysis at the end of a run. The amount of propylene consumed in a run, as calculated from the composition of the oxidation and pyrolysis products, agreed within 10% with the propylene consumption indicated from the observed volume change in the system and the initial and final composition of the gas.

The results of a number of experiments carried out with the recirculation apparatus are summarized in Table I and Table II. The runs were all carried out with high propylene and low oxygen concentrations; the gas at the start of a run was 90% propylene, the remainder being air and carbon dioxide. Oxygen was supplied to the system during the run at approximately its rate of consumption. The average duration of the experiments was four hours.

The experiments in Table I show that under the conditions outlined at temperatures between 500–600° and times of contact of less than eight seconds the oxidation products of propylene are simple in nature. The only oxidation products resulting in amounts sufficient for analysis were acetaldehyde and formaldehyde (grouped as total aldehyde in Table I), formic acid, carbon oxides and water. No evidence was obtained of the presence of propylene oxide or of propionaldehyde which are formed in the oxidation of propylene at lower temperatures.[11] It is probable that

[9] Lenher, Ref. 1, pp. 3744, 3753.

[10] Ref. 6, p. 3356.

[11] Lenher, Ref. 1, p. 3748.

TABLE I

REACTION BETWEEN PROPYLENE AND OXYGEN IN RECIRCULATION APPARATUS USING PACKED PREHEATER AND ONE LITER REACTION VESSEL OF FUSED SILICA

Expt.	Temperature, °C. Reaction vessel	Temperature, °C. Pre-heater	Time of contact, sec.	Initial composition of gas, % C_3H_6	Initial composition of gas, % O_2	Propylene consumed, g.	Yield of products in % of propylene consumed: Oxidation products	Higher olefins	Saturated hydrocarbons
1	518	490	3.7	87.5	0.5 to 1.0 cc./sec. fed in during run	1.88	73.2[a]	26.8	..
2	516	510	7.8	83.8		7.61	38.3[b]	61.6	..
3	500	530	7.8	90.9		7.74	48.0[c]	52.0	..
4	600	585	6.9	91.2		20.61	18.7[d]	52.6	28.6
5	510	502	7.8	91.9	No O_2	0.0	0.0	0.0	0.0
6	590	570	7.0	92.1	No O_2	2.76	0.0	68.1	31.9

[a] Total aldehyde 35.1%
HCOOH 2.0%
CO_2 36.1%

[b] Total aldehyde 16.1%
HCOOH 1.2%
CO_2 21.0%

[c] Total aldehyde 30.1%
HCOOH 1.1%
CO_2 16.8%

[d] Total aldehyde 10.6%
HCOOH 0.3%
CO_2 5.0%
$CO + H_2$ 2.8%

TABLE II

COMPOSITION OF OLEFIN PRODUCTS OF REACTION OF PROPYLENE WITH OXYGEN

Expt.	Composition of olefin products, % of propylene reacted: C_4H_8	C_5H_{10}	C_6H_{12}	Higher members
1	26.8	..	..	..
2	28.5	14.8	55.9	..
3	23.4	23.0	53.6	..
4	9.3	27.4	32.3	30.4[a]
6	17.8	13.2	68.2	..

[a] 11.3 boils 70–85°; 19.1 boils above 85°.

they were formed and were rapidly oxidized and decomposed at the high temperatures of the present experiments.

Experiments 1 to 3 show that in addition to oxidation, pyrolysis of propylene takes place, yielding hydrocarbon products. The only hydrocarbons resulting from this decomposition of propylene at temperatures below 530° are higher olefins, butylenes, amylenes and hexylenes. Experiment 5 with pure, oxygen-free, propylene shows that it is unchanged at 510° and times of contact of eight seconds in a silica vessel. A comparison of Expts. 1 to 3 with Expt. 5 shows that pyrolysis of propylene is effected by oxygen under conditions where pure propylene is thermally stable. This activated pyrolysis of propylene is such an important reaction that with small amounts of oxygen (Expts. 2 and 3) more propylene is pyrolyzed or polymerized, than is oxidized. It is noteworthy that in this activated pyrolysis resulting in the formation of higher olefins there was no formation of oil or tar observed below 600°. At higher temperatures of around

600° saturated hydrocarbons are formed both in the pyrolysis of propylene activated by oxygen (Expt. 4) and in the pyrolysis of oxygen-free propylene (Expt. 6). With pure propylene at 590° over two-thirds of the products of pyrolysis are olefins and one-third is saturated hydrocarbons with two carbon atoms in the molecules and with propylene activated by oxygen at 600° of the hydrocarbon products 64.8% is higher olefins, and 35.2% is saturated hydrocarbons with two carbon atoms in the molecule. As higher mono-olefins are the only hydrocarbon products of the pyrolysis of propylene activated by oxygen at 500°, it can be concluded that higher mono-olefins are the primary products of the pyrolysis of propylene and that the saturated hydrocarbons formed at higher temperatures are the result of secondary decompositions of the primary products.

The higher olefin reaction products were dried over solid potassium hydroxide and distilled from fresh potassium hydroxide. They were water-white limpid liquids of density less than 1. They had the characteristic olefinic odor, they absorbed bromine forming liquid bromides, decolorized permanganate solution rapidly in the cold, and were insoluble in water. The dried mixture of hydrocarbons was fractionated in a small still. The fraction boiling from −6 to 0° was assumed to be butylene, after the above chemical tests. In Expts. 1, 2 and 3 sharp fractions at −6° to 0°, 30–38° and 60–65° were the only products. The fraction boiling from 30–38°, where the amylenes boil, was assumed to be amylenes. On microcombustion the composition of this fraction was found to be C = 87.25%, H = 12.71%; theoretical for C_nH_{2n} is C = 85.7%, H = 14.3%. The fraction boiling from 60–65°, where the hexylenes boil, was assumed to be hexylenes. This fraction on microcombustion showed its composition to be: C = 86.71%, H = 12.41%. In Expt. 4 at 600° the dried hydrocarbon products recovered from the absorbent charcoal, after distilling off butylenes (−6 to 0°) boiled over the range 30 to 85° with two main fractions at 30–40° and 60–69°. The 30–40° fraction analyzed C = 87.85%, H = 11.27%, and the 60–69° fraction analyzed C = 87.90%, H = 11.41% by microcombustion. Redistillation of these fractions from solid potassium hydroxide and storing over anhydrous magnesium sulfate did not change the analysis. The boiling ranges of the various fractions together with their physical and chemical properties show that they were olefin hydrocarbons. The fractions probably contained small amounts of dienes, as 1,3-pentadiene b. p. 42°, 2,3-pentadiene b. p. 49–51°, and 1,3-hexadiene b. p. 72–74°, which would change the ratio for carbon to hydrogen from the theoretical for C_nH_{2n} in the direction of the higher carbon and lower hydrogen percentages found by analysis. There was no evidence of the formation of detectable amounts of cycloparaffins.

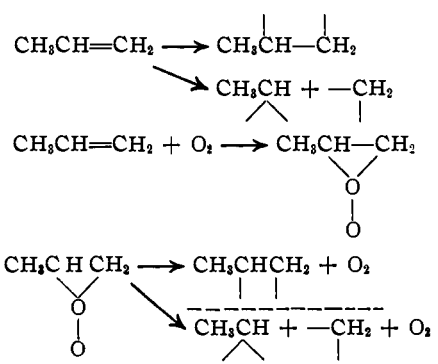
A check on the entire experimental procedure was made by filling the system with propylene, saturating the charcoal and circulating the gas

with the reaction vessel at room temperature. The charcoal was then removed and heated to 140° and steamed. No liquid hydrocarbons, other than propylene, were separated in the recovery system. It is clear that the hydrocarbons recovered after an experiment had been formed in the reaction and had not come from the original propylene as contamination or been formed from propylene in the absorbent charcoal on recovery.

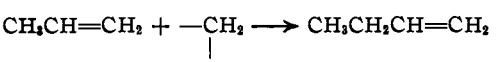
Discussion

These experiments show that propylene containing small amounts of oxygen undergoes a polymerization reaction as well as oxidation and that the primary products of this polymerization are higher mono-olefins. The data show further that oxygen activates this pyrolysis of propylene to take place more rapidly at a lower temperature than is the case in its absence.

Since the pyrolysis of propylene activated by oxygen takes place in its initial stages without separation of carbon or hydrogen or formation of saturated hydrocarbons, the occurrence of mono-olefin products must be due to an activation of the hydrocarbon which will allow it to react with itself without changing the ratio of carbon to hydrogen. This activation consists in an opening up of the double bond by heat, or oxygen. It has been shown in the similar behavior of ethylene that this activation may lead to the formation of activated hydrocarbon molecules by the breaking of one of the carbon double bonds, and to the separation of methylene radicals by a scission of the two carbon double bonds; these considerations[12] may be taken to apply without modification to the oxidation, activation and polymerization of propylene. The first step in the reaction is an activation of the double bond by heat or oxygen



Butylene is formed by a reaction of a methylene radical with propylene



(3)

[12] Lenher, Ref. 1, p. 3756.

The amylenes may be formed in a reaction between an ethylidene residue and propylene

$$CH_3CH + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_2CH{=}CH_2 \qquad (4)$$

As both butylenes and amylenes occur in amounts which are smaller than the amount of hexylene, the formation of hexylene is the most important reaction. Hexylene is formed in the reaction of an activated propylene molecule with a normal propylene molecule, as

$$CH_3CH{-}CH_2 + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_2CH_2CH{=}CH_2 \qquad (5)$$

This reaction presents certain theoretical difficulties as it is a bimolecular association reaction, but it appears from a recent speculation of Kassel[13] that such reactions are possible.

This outline of the activation and pyrolysis of propylene explains satisfactorily the observed products and the probable mechanism of the primary processes involved. Recent investigators of the pyrolysis of propylene[3,4,5] have concluded that the principal primary products are other than those obtained in the present work. These results of other investigators are not actually in conflict with the present findings; they show that these authors were not dealing with the primary products of the pyrolysis of propylene but that the products which they obtained were the result of a more profound decomposition which carried the pyrolysis beyond the primary stage. The present experiments carried out at low temperatures and short times of contact have enabled the isolation of the primary products to be made. Wheeler and Wood's own work[4] on the pyrolysis of the butylenes shows that when they break down at 600° at longer times of contact than were used in this paper, they yield propylene, ethylene, ethane, methane and hydrogen, and it may be assumed that the C_5 and C_6 olefins yield similar simple products under the same conditions. This pyrolysis of higher mono-olefins formed as the primary products on heating a longer time accounts for the simpler olefin and paraffin hydrocarbon products obtained by Frey and Smith, Wood and Wheeler and Hurd and Meinert. It is evident, therefore, that the primary products of the pyrolysis of propylene are higher mono-olefins and that ethylene, simple paraffins and hydrogen result from secondary reactions. The formation of aromatics occurs only above the temperature range considered in this paper.

The similarity between the behavior of ethylene and of propylene in their oxidation and pyrolysis reactions shows that the mechansim of these reactions which has been outlined above and in a previous paper[12] is general for the mono-olefin series of hydrocarbons.

[13] Kassel, THIS JOURNAL, **53**, 2143 (1931).

Summary

The reaction between propylene and oxygen at high propylene and low oxygen concentrations has been studied in a recirculation apparatus between 500 and 600°. In addition to oxidation of propylene, pyrolysis of propylene takes place.

The oxidation products were acetaldehyde, formaldehyde, formic acid, carbon oxides and water.

The primary products of the pyrolysis were higher mono-olefins, butylenes, amylenes and hexylenes. Secondary products of pyrolysis are olefins, paraffins and hydrogen.

The temperature at which pyrolysis of pyropylene is appreciable is lowered greatly by the presence of small amounts of oxygen, and the rate of pyrolysis is markedly increased.

A mechanism of the oxidation and pyrolysis of propylene based on the activation of the carbon double bond has been outlined.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 307]

THE GAS PHASE EQUILIBRIUM BETWEEN METHYL NITRITE, HYDROGEN CHLORIDE, METHYL ALCOHOL, AND NITROSYL CHLORIDE. THE ABSORPTION SPECTRUM OF NITROSYL CHLORIDE

BY J. A. LEERMAKERS AND H. C. RAMSPERGER

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Free energy values of organic substances will probably most often be obtained from heats of combustion and specific heat data by use of the third law of thermodynamics. They may, of course, be obtained with considerable accuracy from equilibrium data, but often a good equilibrium free from side reactions cannot be obtained with organic compounds. It is still more unusual to establish a gas phase equilibrium at room temperature. In the course of an investigation by the junior author to locate a gas phase reaction suitable for reaction rate research it was found that an equilibrium was very rapidly established between the gases listed in the title at room temperature. This was shown by the immediate partial disappearance of the color of nitrosyl chloride gas when added to an excess of methyl alcohol gas, and the appearance of the same color when hydrogen chloride gas was added to methyl nitrite gas. The thermodynamic data for the three gases, methyl alcohol, nitrosyl chloride and hydrogen chloride are quite accurately known so that from equilibrium measurements at two temperatures we are able to calculate the free energy of formation, the heat of formation and entropy of methyl nitrite.