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The Reaction between Oxygen and 2-Butene

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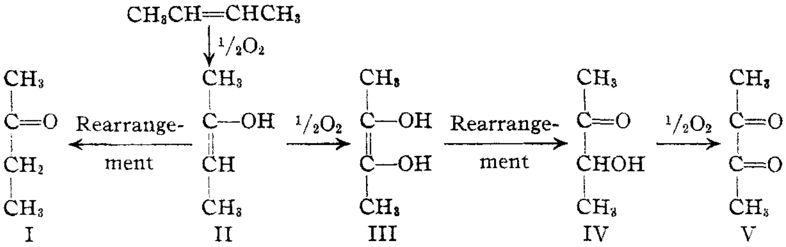
Introduction

Early in his investigations of the autoxidation of hydrocarbons Bone extended his hydroxylation theory to include unsaturated hydrocarbons.[1] He contended that the first step in the reaction between oxygen and ethene was the formation of vinyl alcohol, since acetaldehyde was isolated as a reaction product. Bone[2] has recently reiterated his belief in the hydroxylation mechanism as applied to ethene. However, he now recognizes that ethene oxide is also present, in agreement with Lenher,[3] who has shown that an olefin oxide is formed in the reaction between ethene (or propene) and oxygen, but Bone regards the oxide as arising from vinyl alcohol. It is evident, then, that there are two possible precursors of acetaldehyde in the ethene oxidation, *viz.*, vinyl alcohol and ethene oxide, the first resulting from a reaction of hydroxylation according to the mechanism of Bone, the second arising from an oxidation of ethene to ethene oxide according to Lenher. Although Lenher believes that the ethene oxide is formed by a reaction of ethene peroxide with ethene, producing two moles of the oxide from one mole of each of the other two, it is possible that ethene oxide could result from ethene by the action of some other peroxide, for example a peroxy acid.



PREDICTED OXIDATION PRODUCTS OF 2-BUTENE VIA THE MECHANISM OF HYDROXYLATION

By studying the reaction between oxygen and 2-butene it should be possible to obtain more definite evidence in regard to the oxidation mechanism. If hydroxylation takes place at either one of the two unsaturated carbon atoms, methyl ethyl ketone (I) should be one of the reaction products, or if hydroxylation takes place at both of the unsaturated carbon atoms,[4] dimethylglycolic aldehyde (IV) or its oxidation product dimethylglyoxal (V) should be present.

Using 2,4-dinitrophenylhydrazine as the reagent for oxo compounds the hydrazone of acetaldehyde and the osazone of glyoxal were the only derivatives of oxo compounds which could be isolated. There was no indication that the hydrazone of methyl ethyl ketone or the osazone of dimethylglyoxal[5] was present in the reaction product with 2,4-dinitrophenylhydrazine. The possibility of hydroxylation proceeding at a terminal carbon atom can be rejected, since this would lead to the production of crotonic aldehyde, none of which was found in the reaction mixture. From these statements it is fairly certain that hydroxylation is *not* an important factor in the oxidation of 2-butene under the experimental conditions.

Experimental

In order that intermediate oxidation products could be isolated the flow method was used and the molal ratio of butene to oxygen was always greater than unity.

Materials.—The 2-butene, obtained from 1-butanol and sulfuric acid,[6] was purified by passing through three spiral wash bottles, the first two containing 40% sulfuric acid solution and the last one 50% potassium hydroxide, and then through a tower containing soda-lime and calcium chloride. It was collected in a trap at −20°. This was sealed off until the butene was needed. The oxygen was taken from a tank and was approximately 99–99.5% pure. The desired butene–oxygen mixture was made by displacing the proper volume of brine in a 20-liter bottle. After standing overnight this mixture was driven into the bottle D (Fig. 1) just before a run was started. The composition was determined by analyzing a sample for butene by absorption in concentrated sulfuric acid and for oxygen by absorption in alkaline pyrogallol.

Apparatus.—This is shown in Fig. 1. A to H represents a satisfactory device for delivering gas at a constant rate. AB and BC are 14-mm. tubes, the former projecting about 100 cm. above the top of the 20-liter bottle D. At the

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(1) Bone and Wheeler, *J. Chem. Soc.*, **85**, 1637 (1904).

(2) Bone, *ibid.*, 1599 (1933).

(3) Lenher, THIS JOURNAL, (a) **53**, 3737 (1931); (b) **53**, 3752 (1931); (c) **54**, 1830 (1932).

(4) Bone states that the oxidation process, in the case of ethene, proceeds rapidly through the monohydroxy stage to a dihydroxy stage.

(5) Both IV and V would yield this osazone.

(6) Young and Lucas, THIS JOURNAL, **52**, 1964 (1930). The sulfuric acid should be 60% by volume.

point B a 5-cm. piece of 1-mm. capillary tubing is fitted between the tubes AB and BC. Just below B is a pinhole, P. H., by which the pressures in D and BC are equalized. Water completely fills the tube AB, the excess flow going to the sink, and the 100-cm. column constitutes a constant head to force the gas through the apparatus against the back pressure of the wash bottles. The rate of flow is regulated by the needle valve, F.

During a run, the gas passed through the calcium chloride tower, E, and needle valve, F, through a flowmeter, G, into the reaction tube, H, heated in an electric furnace, J, and provided with three equally spaced, chromel–alumel thermocouples, K-1, K-2 and K-3. The exit gases, after passing through the short condenser, L, and ice trap, M, entered the two spiral wash bottles, N-1 and N-2, filled with water, then into the three traps, O-1, O-2 and O-3, the first one at −15 to −20° (ice–hydrochloric acid) and the last two at −80°, and finally into the balloon, P. Thus the reaction products would be collected as follows: in M, easily condensable substances such as water or polymerized products, in N the water-soluble products such as aldehyde, in O, the unchanged butene and in P the non-condensed gases such as oxygen and oxides of carbon.

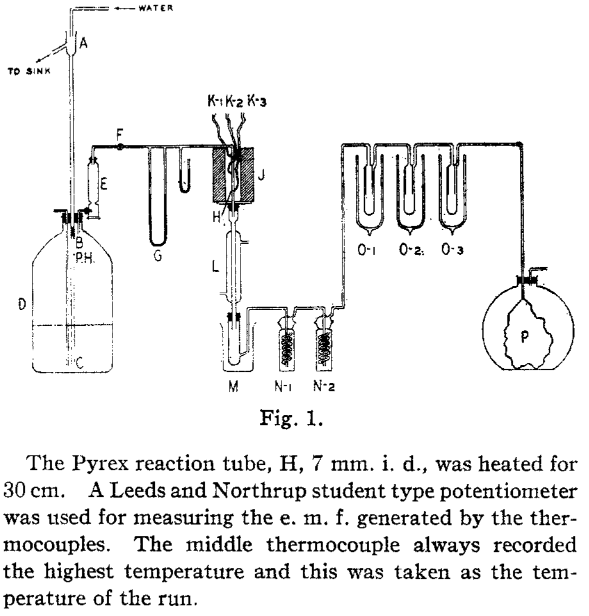

Fig. 1.

The Pyrex reaction tube, H, 7 mm. i. d., was heated for 30 cm. A Leeds and Northrup student type potentiometer was used for measuring the e. m. f. generated by the thermocouples. The middle thermocouple always recorded the highest temperature and this was taken as the temperature of the run.

Runs were carried out at different temperatures but other conditions were kept as non-variant as possible. The four satisfactory runs were made at 375, 415, 456 and 490°. The butene–oxygen ratio was always slightly greater than unity and the rate of flow of the butene–oxygen mixture varied from 60 to 65 cc. per minute. The duration of each run was approximately three hours.

Reaction Products

Butene and Butadiene Condensate.—The liquid in traps O-1, O-2 and O-3 was a mixture of the two condensed gases. The composition was determined by conversion to the corresponding di- and tetrabromides by distilling the gas through a 20-cm. column of bromine kept dark and cooled to a temperature of −5 to −15°. The operation was carried out in an all-glass apparatus without loss of butene. The bromine was purified by treatment with saturated aqueous potassium bromide followed by washing with water and distillation from concentrated sulfuric acid. The mixture of di- and tetrabromobutanes, after removal of excess bromine and drying with anhydrous calcium chloride, was quantitatively separated by a fractional distillation at 50 mm. through a vacuum-jacketed Vigreux column after the design of Weston.[7] The dibromobutane distilled over and the butadiene tetrabromide, which remained behind in the still, crystallized on cooling. After one crystallization from alcohol, this melted at 115° and mixed melting point with known butadiene tetrabromide established its identity.

Ice-trap Condensate.—At temperatures below 450° a very small amount of a one-phase, aqueous liquid condensed at 0° while at higher temperatures a larger amount of aqueous condensate and a smaller amount of a yellow oil of density about 0.9 was present. The amount of oil formed was measured volumetrically. Because of the small volume, the amount of oil measured was less than the total, due to the fact that some remained on the walls of the collecting tube. The percentage lost in this way was greatest for the smallest volumes. Both phases had strong, pungent odors, gave positive tests for peroxide with titanium tetrachloride in dilute hydrochloric acid, gave good iodoform tests, reacted acid to litmus and rapidly decolorized a solution of bromine in carbon tetrachloride. The bromine absorption number of the oil, determined by means of standard bromate–bromide solution, indicated a molecular weight of 124–125. This suggests that the oil was largely octene (mol. wt. 112) formed by polymerization of the butene.

The aqueous phase gave a positive qualitative test for formic acid when heated with powdered mercuric oxide[8] and a positive olefin oxide test with a saturated solution of manganous chloride.[3a] On standing, the acidity of the aqueous phase increased and a gas was observed to be evolved in some cases. Lenher[3a] records a similar change in the oxidation products of ethene and ascribed it to the presence of dihydroxydimethyl peroxide, $HOCH_2OOCH_2$-OH. However, a peroxide and an aldehyde alone could account for this change, since an aqueous solution of hydrogen peroxide, formaldehyde and sulfuric acid[9] or one of hydrogen peroxide, paraldehyde and sulfuric acid[10] becomes more acidic on standing and at the same time evolves a gas.

A rough estimate of the amount of acid, peroxide and olefin oxide in the condensate was obtained by the following procedure. The acidity was determined by quickly titrating an aliquot of the condensate with 0.1 *N* sodium hydroxide at or near 0°, using phenol red as the indicator. Even at this low temperature the end-point shifted slowly, due to a slow formation of acid. The peroxide was determined by adding an excess of 0.1 *N* sodium hydroxide to the neutralized portion above and letting the mixture stand for about four days at 10°, during which time aldehyde, which was present in large excess, was oxidized to acetic acid by the peroxide. Back titration of the excess base

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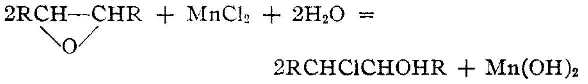
[7] Weston, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

[8] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1904, Vol. I, p. 83.

[9] Fry and Payne, THIS JOURNAL, **53**, 1973 (1931).

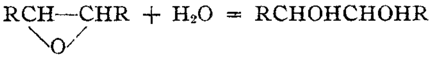
[10] Fry and Payne, *ibid.*, **53**, 1980 (1931).

gave the amount of acid formed, consequently the amount of peroxide reduced. Olefin oxide was then determined on the same solution by adding solid manganous chloride to the neutralized solution, letting this stand at room temperature for several days and then titrating the manganous hydroxide formed



$$2\mathrm{RCH}\underset{\mathrm{O}}{\text{—}}\mathrm{CHR} + \mathrm{MnCl_2} + 2\mathrm{H_2O} = 2\mathrm{RCHClCHOHR} + \mathrm{Mn(OH)_2}$$

For this titration phenol red was quite satisfactory whereas methyl orange and phenolphthalein were not. It is probable that the value obtained for the olefin oxide content is low since even in alkaline solution there is a slow disappearance of an olefin oxide[11]



$$\mathrm{RCH}\underset{\mathrm{O}}{\text{—}}\mathrm{CHR} + \mathrm{H_2O} = \mathrm{RCHOHCHOHR}$$

No great accuracy is claimed for the determination of peroxide by this procedure, since dismutation of aldehyde may possibly take place under the alkaline conditions. Values were obtained for the peroxide at 456 and 490° and for the olefin oxide at 405 and 456° but the results are here reported merely as qualitative since the values were so small.

Wash Water.—This contained aldehyde. The aldehyde content of aliquots of the aqueous condensate and wash water was determined by conversion to the dinitrophenylhydrazone. Since the derivatives of only two aldehydes could be isolated, the hydrazone of acetaldehyde and the osazone of glyoxal, it was possible to obtain a close approximation to the amount of each of these aldehydes since these derivatives can be separated completely from each other with but little loss by repeated crystallization from dilute alcohol. Although formaldehyde can be detected, when in the presence of a much larger amount of acetaldehyde, by selective precipitation with *p*-nitroaniline,[12] its presence in the aqueous solutions could not be established by this means.

Separation and Identification of the Aldehydes.—The procedure of Brady[13] was followed in reaction of the aldehydes with 2,4-dinitrophenylhydrazine. An aliquot of the precipitated hydrazones was fractionally extracted with and crystallized from alcohol, giving two fractions: (a) a relatively insoluble osazone of glyoxal and (b) a relatively soluble hydrazone of acetaldehyde. When pure, the former melted at 318–320° with decomposition, and at 317–319° when mixed with known osazone (m. p. 322°). The acetaldehyde derivative melted sharply, after purification from alcohol-water mixtures, at 150–151° and this value was not depressed when mixed with a known sample (149–150°). Since the main portion of the hydrazone was readily purified by repeated crystallizations from dilute alcohol and since there was no indication of the presence of other hydrazones, it is reasonable to believe that other oxo-compounds were absent, or at best present in small amounts. As a further check on the absence of other hydrazones,[12] a solution of the crude hydrazone in carbon tetrachloride was passed through a 25-cm. column of a mixture of powdered alumina[14] and diatomaceous earth (the latter to facilitate filtration). Using this procedure, it was possible to separate into bands, known mixtures of the 2,4-dinitrophenylhydrazones of acetaldehyde and propionaldehyde containing amounts of the latter as low as 15%. The crude hydrazone solution gave no evidence of more than one band. The glyoxal osazone is relatively insoluble in carbon tetrachloride and did not interfere with this test.

Other compounds which it was thought might be present, but of which no trace could be found, were the 2,4-dinitrophenylhydrazones of formaldehyde, propionaldehyde, *n*-butyraldehyde, isobutyraldehyde, crotonic aldehyde and methyl ethyl ketone.

Non-condensed Gases.—The collection of these gases was not started until the air was completely swept out of the apparatus, or until about one-sixth of the butene–oxygen mixture had been passed. Consequently the amounts reported are low by 15–20%. These gases, which were caught in the rubber balloon, were analyzed, those from the 375, 415 and 476° runs in an Orsat gas analysis apparatus, and the 490° run in a Podbielniak column, the latter for the purpose of obtaining data on the presence of methane, ethane and propane. The first of these paraffins was present and the latter two were absent.

Packed-tube Experiments.—When the reaction tube was packed with glass wool no aldehyde could be detected in the wash water when the furnace was kept at 375° (a temperature at which reaction takes place in the empty tube), while at 455° the aldehyde reactions were faint and the peroxide test was negative, whereas these tests were strongly positive when the tube was empty. Only a very few small crystals of butadiene tetrabromide were observed in the packed tube experiment at 455°, about one-twentieth of the amount obtained when the tube was not packed. The suppression of the reaction when the tube was packed is similar to the behavior of ethene and propene.[3] The total recovery of butene was 97% of the amount passed. Of the 3% unrecovered the larger part was lost in the apparatus and wash waters since the amount reacted was insignificant.

Discussion of Results

Table I gives the composition of the entering butene–oxygen mixture and of the non-condensed reaction gas, while in Table II are shown the amounts of reaction products. In Table III the results have been recalculated on the basis of moles of butene passed through the reaction tube.

At the lowest temperature, 375°, a slow reaction took place and at higher temperatures the oxidation proceeded more rapidly. The nature of the oxidation seemed to change in the vicinity of 450°, while at 490° the reaction was very close to a combustion. Above 500° much soot was formed. The comparatively small increase in the amount of aqueous condensate and the comparatively large increase in the amount of oil

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[11] Brönsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

[12] Suggested by H. H. Strain, Carnegie Institution of Washington, Stanford University, California.

[13] Brady, *J. Chem. Soc.*, 756 (1931).

[14] Activated Alumina, Grade A, Aluminum Ore Co., East St. Louis, Ill. This was powdered and sieved through a 65-mesh screen.

TABLE I

ANALYSIS OF GASES

Temp., °C.	Av. rate of flow, cc./min.	Entering gas				Exhaust gas, %							
		C_4H_8, %	O_2, %	N_2, %	C_4H_8, Moles	Moles	C_4H_8	H_2	CO	CO_2	O_2	N_2	CH_4
375	65.0	58.7	39.0	2.3	0.3265	0.1904	0.91	0.45	0.62	0.25	89.8	7.8	
415	62.3	55.2	40.1	4.7	.2650	.1265	.94	2.0	.81	.47	85.1	10.9	
456	59.3	53.6	39.4	7.0	.2660	.1069	.90	0.0	3.3	1.5	83.8	10.5	
490	65.0	56.4	41.4	2.2	.2925	.1328							2[a]

[a] C_2 and C_3 hydrocarbons absent, some C_4 present.

TABLE II

ANALYSIS OF CONDENSABLE PRODUCTS

Temp., °C.	$C_4H_8Br_2$		$C_4H_6Br_4$		Ice-trap condensate			2,4-Dinitrophenylhydrazones		Acid equivalents	Peroxide	Olefin oxide
	G.	Mole	G.	Mole	Water, ml.	Oil, Ml.	Oil, Mol. wt.	Moles as CH_3CHO	$(CHO)_2$ %			
375	66.5	0.308	1	0.003	...	...	...	0.00464	Trace	+	−	+
415	51.6	.239	1.4	.0038	0.1	...	...	.0127	2–3	0.0054	+	+
456	43.3	.208	1.9	.0051	1.2	0.3	125.0	.0379	8–12	.0053	+	+
490	46.4	.215	3.5	.0094	1.7	.9	124.2	.0421	3–5	.0013	+	+

TABLE III

MOLES PRODUCT PER MOLE OF BUTENE PASSED

Temp., °C.	$C_4H_8Br_2$	C_4H_8		C_4H_6	C_8H_{16} crude	Aldehydes		Acid	CO	CO_2	H_2	CH_4
		Exit gas	reacted			CH_3CHO	$(CHO)_2$					
375	0.944	0.005	0.051	0.008	+	0.014	Trace	+	0.0036	0.0015	0.0025	
415	.902	.004	.094	.016	+	.047	0.001	0.020	.0039	.0022	.0096	
456	.782	.004	.214	.019	0.008	.129	.008	.021	.0135	.0059	.0009	
490	.735	.004[a]	.261	.032	.022	.138	.003	.004				0.01

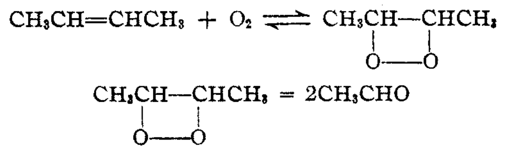
[a] Estimated.

condensate or polymer (Table II) between 456 and 490° indicated that polymerization became more important at temperatures above 450°. The absence of appreciable amounts of ethane, ethene, propane and propene in the gas from the 490° oxidation (Table I) was demonstrated by distillation through a Podbielniak column.

This result indicated that propionic, acrylic, butyric and crotonic aldehydes could not have been formed in appreciable amounts during this oxidation. The 2% of methane in the exit gas can be accounted for as coming from acetaldehyde through pyrolysis. At the lowest temperature, 375°, the amounts of acid, peroxide and olefin oxide were so small that satisfactory analytical data could not be obtained. In Table III the amount of butene reacted was calculated from the difference between that passed and that recovered, taking into account the fact that 3% was lost in the apparatus.

Reaction Mechanism.—Except for the conclusion that hydroxylation was not an important factor in the reaction between 2-butene and oxygen, it is not possible to say definitely that the reaction proceeded by a given mechanism. However, it seems worth while to discuss a plausible course which is indicated by the nature of the reaction products.

In order to account for the predominatingly large proportion of acetaldehyde in the reaction product at all temperatures, it seems reasonable to believe that the oxidation proceeds through the formation of a peroxide[15] and the decomposition of this into two molecules of acetaldehyde



$$CH_3CH{=}CHCH_3 + O_2 \rightleftharpoons \underset{\displaystyle O\text{—}O}{CH_3CH\text{—}CHCH_3}$$

$$\underset{\displaystyle O\text{—}O}{CH_3CH\text{—}CHCH_3} = 2CH_3CHO$$

Using the bond energies of Pauling[16] and of Pauling and Sherman,[17] 5.09 v. e. for the oxygen molecule,[16] and a value of −0.3 v. e. for the four-membered ring, the calculated energy decrease for the formation of the peroxide from butene and oxygen is approximately 0.2 v. e. The energy decrease for the decomposition of the peroxide is approximately 3.27 v. e. (74 kg. cal.). From data on heats of combustion, there is an over-all energy change of 87 kg. cal. It would be expected that a peroxide molecule would decompose into two acetaldehyde molecules and that these would carry the energy of the reaction. If the

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[15] Stephens, THIS JOURNAL, **50**, 568 (1928), has isolated cyclohexene peroxide; Hyman and Wagner, *ibid.*, **52**, 4345 (1930), have shown that peroxides are formed between the pentenes and oxygen.

[16] Pauling, THIS JOURNAL, **54**, 3570 (1932).

[17] Pauling and Sherman, *J. Chem. Phys.*, **1**, 607 (1933).

energy is divided equally, each will have a minimum activation of 37 to 43.5 kg. cal. which is close to the observed activation energy of 45 kg. cal.[18] Part of the aldehyde therefore will be expected to decompose into carbon monoxide and methane,[19] as it picks up additional energy. The observed decomposition is small, about 10%.

According to the proposed mechanism, Fig. 2, the first step in the oxidation would be the formation of the unstable butene peroxide, which would decompose into acetaldehyde. Most of this could pass through unchanged, a part would decompose into methane and carbon monoxide and another part combine with oxygen to form peroxyacetic acid.[20] This in turn would react with 2-butene to form butene oxide and acetic acid,[21] and the resulting butene oxide could decompose into butadiene and water.[22] Oxygen may attack the double bonds of butadiene and cause a scission at these positions to formaldehyde and glyoxal, analogous to scission of 2-butene to acetaldehyde. The formaldehyde in part decomposes into hydrogen and carbon monoxide[23] and in part undergoes oxidation, presumably to peroxyformic acid, which in turn would either decompose to carbon dioxide and water, as shown, or react with butene to produce butene oxide and formic acid. The glyoxal, either in whole or in part, passes through unchanged. Butene oxide may possibly arise, not only from the action of a peroxy acid upon butene, but also from its reaction with butene peroxide, as proposed by Lenher[3] for ethene. However, this does not seem to be important except at the highest temperatures, where the mechanism was more complicated.

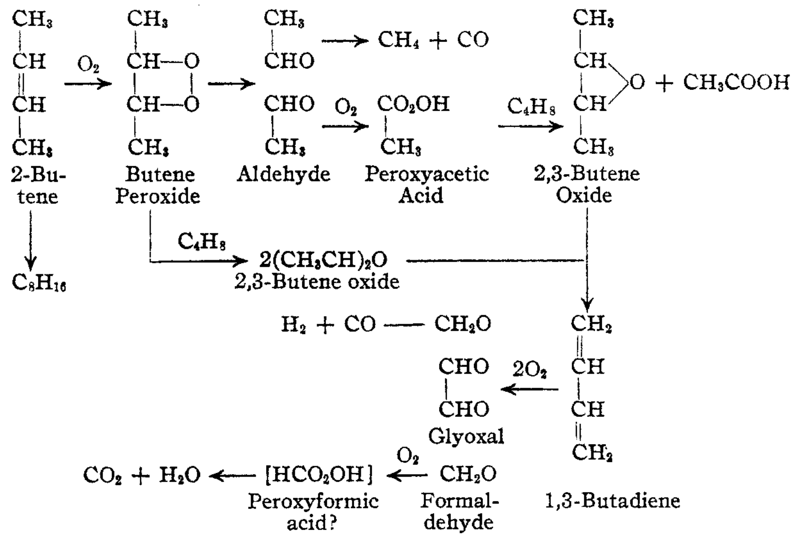

Fig. 2.—Mechanism of 2-butene–oxygen reaction.

The proposed mechanism accounts in a simple fashion for certain facts, as follows: (a) acetaldehyde was the principal reaction product at all temperatures; (b) butadiene was always formed, even at the lowest temperature; (c) the amount of aldehyde always exceeded that of butadiene which in turn exceeded the glyoxal; (d) at 415 and 456°, the amount of acid found was somewhat more than the amount of butadiene.

Summary

When a mixture of 2-butene and oxygen, butene in excess, was passed through a hot tube at 375, 415, 456 and 490°, the principal reaction products in all cases were acetaldehyde and butadiene, less important products were glyoxal (or glycolic aldehyde), an olefin oxide, an acid (or acids) and some peroxide. At the higher temperatures octene was formed by a polymerization reaction.

Hydroxylation is not important in the oxidation of 2-butene for no methyl ethyl ketone was formed. If hydroxylation were the first step in the oxidation, this ketone should result from the rearrangement of 2-butene-2-ol.

A probable reaction mechanism assumes the formation of 2-butene peroxide which decomposes into acetaldehyde. The other products are thought to result from a succession of reactions already known.

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[18] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932, p. 72.

[19] Bone and Stocking, *J. Chem. Soc.*, **85**, 727 (1904).

[20] At 25° acetaldehyde and oxygen under a pressure of 0.1 atmosphere produce peroxyacetic acid. Von der Hellen, Paetsch, Titschack and Lange, *Ber. Berlin Akad.*, 72 (1931); see Bodenstein, *Z. physik. Chem.*, **12B**, 151 (1931).

[21] Olefin oxides result from the action of peroxy acids upon olefins; Prileschajew, *Ber.*, **42**, 4811 (1909); Lenher, Ref. 3.

[22] Kyriakides, THIS JOURNAL, **36**, 663 (1914), found that olefin oxides yield butadiene hydrocarbons when in contact with kaolin at 350° under reduced pressure.

[23] Bone, *J. Chem. Soc.*, **87**, 910 (1905).