

THE ISOMERIC 2-PENTENES
THE REACTION BETWEEN OXYGEN AND 2-BUTENE

Thesis by
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This thesis consists of the following parts:

I. Acknowledgment.

II. "The Isomeric 2-Pentenes"

III. "The Reaction Between Oxygen and 2-Butene"

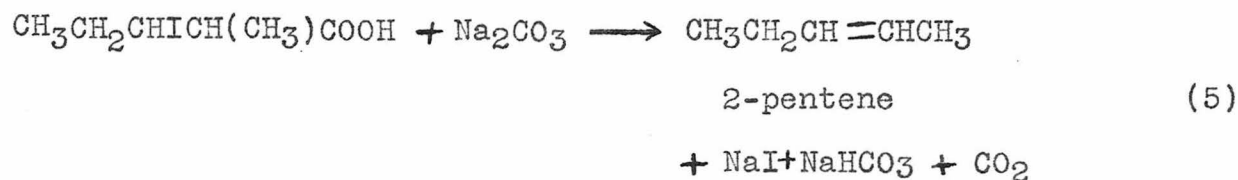
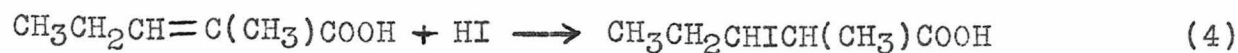
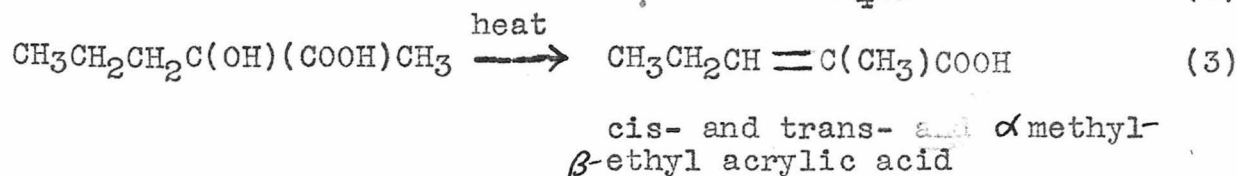
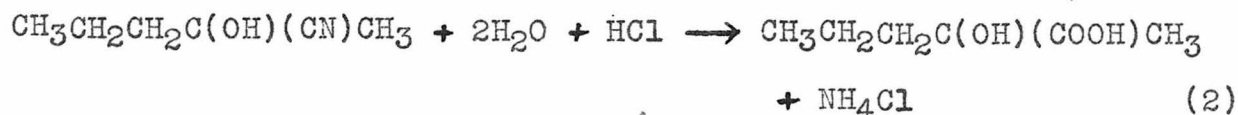
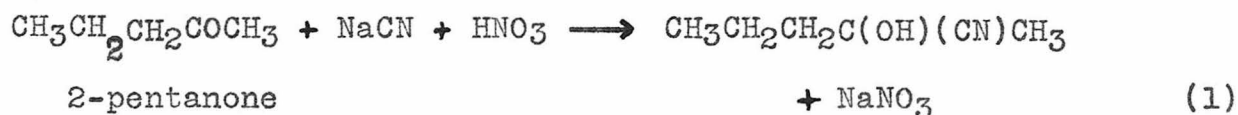
ACKNOWLEDGMENT

I gratefully acknowledge my great debt to Professor Howard J. Lucas, both for valuable advice and criticism and for a warm friendship which has done much to make my stay at the Institute an exceedingly pleasant one.

THE ISOMERIC 2-PENTENES

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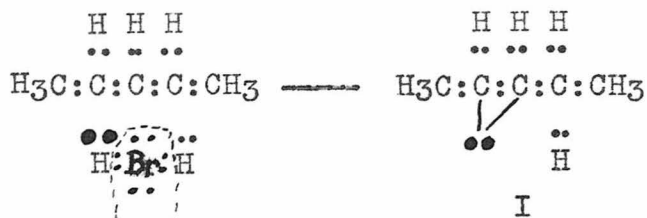
This report contains the results of an investigation into the properties of the pure isomeric cis- and trans- 2-pentenes in an effort to check the validity of certain statements made by Kharasch and co-workers¹ and supported by Sherrill and co-workers². For this purpose, it was necessary to synthesize the two isomers by a method which would unquestionably lead to the pure forms. The method used was similar to the one described by Wislecenus, Talbot, Henze and Schmidt³ as modified by Young, Dillon and Lucas⁴ for the synthesis of the isomeric 2-butenes. The following equations illustrate the reactions involved:



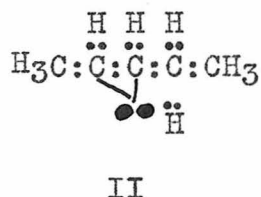
The only previous attempts to prepare the pure cis- and trans-2-pentenes involved fractional distillation of 2-pentene mixtures. Van Risseghem⁵ could get no evidence of separation after repeated fractionations and concluded that only one form was stable or that the two forms were in equilibrium. This is in agreement with the work done in this laboratory as the 2 isomers were found to have the same boiling points.

Kharasch¹, in connection with his theory of the partial polarity of the ethylene bond, found it necessary to postulate the existence of "electromeric isomerism" to explain the course of the addition of hydrogen bromide to 2-pentene and to bring it into agreement with his theory of the nature of the ethylene bond. According to Kharasch, 2-pentene should add hydrogen bromide to give largely 2-bromopentane, whereas Lucas and Moyses⁶ predicted the product to be largely 3-bromopentane. Actually it was found that the product of the reaction was 22% 2 bromo- and 78% 3-bromopentane. The following quotation⁷ illustrates the mode of formation of "electromers" and the reasoning which led Kharasch to postulate their existence:

"A careful analysis, however, of Lucas and Moyses's method of preparing the 2-pentane revealed the fact that since the 2-pentene is prepared from 3-bromopentane the following might represent the course of the reaction:



The bromide ion is removed by the alcoholic potassium hydroxide, the hydrogen ion drops off to maintain the electrical neutrality of the molecule and unsaturated derivative of Form I would be produced. Also, since the methyl radical is only slightly more electronegative than the ethyl radical, the rearrangement to Form II,



the most stable condition, would only be a slow one, and that might account for the addition of HBr as observed by Lucas and Moyse and confirmed by us. The possibility then suggested itself that, by applying a "strain" to the system, the transition might be expedited."

Kharasch found that light or heat treatment of 2-pentene prepared from 3-bromopentane changed the course of the addition reaction with hydrogen bromide. At Kharasch's request, Sherrill, Carr, and co-workers^{2abc} undertook the preparation of 2-pentene and a study of its reactions with hydrogen bromide and bromine and of its absorption spectra. They found, in agreement with Kharasch, that 2-pentene, prepared by action of potassium hydroxide in absolute methanol upon 3-bromopentane, reacted with hydrogen bromide

in glacial acetic acid to give 78% 3-bromo- and 22% 2-bromopentane while the same 2-pentene after exposure to sunlight gave 15% 3-bromo- and 85% 2-bromopentane.

Recently, however, Lauer and Stodola⁸ have reported on the addition of hydrogen bromide to 2-pentene prepared in two different ways, viz: from 3-bromopentane according to the method of Sherrill, Otto, and Pickett^{2a} and from α -ethylcrotonic acid through a synthesis similar to the one used in this paper. These preparations allowed Lauer and Stodola to duplicate the work of Sherrill and co-workers and to investigate the addition of hydrogen bromide to the trans geometrical isomeride prepared in pure form by their method. Using an analytical method based upon conversion of the bromides into the anilides, claimed by the authors to be the most accurate method of analysis, Lauer and Stodola found that nearly equivalent amounts of the 2-bromo and 3-bromopentane were formed, irrespective of the 2-pentene stated with. These results are in disagreement with results given earlier in this paper and led Lauer and Stodola to conclude that ⁹ "current views, concerning electromeric displacement in pentene-2 must be modified and the theory of partial polarity is invalidated insofar as it derives support from the previous studies of the behavior of pentene-2" upon the addition of hydrogen bromide."

Sherrill^{2b} also prepared 2-pentene from 2-bromopentane and, after careful fractionation to remove

any 1-pentene present, obtained a compound differing slightly in physical properties from the product obtained from 3-bromopentane but corresponding somewhat closely to the pentene from 3-bromopentane after exposure to light.

Upon reaction of these pentene samples with bromine, Sherrill found that the different 2-pentene samples gave dibromides with the same refractive index and assumed therefrom that the two isomers were not cis- and trans-isomers but "electromers" as she considered that cis-trans isomers would give two dibromides, a meso and a dl mixture, having different refractive indices. Contrary to her suppositions, however, the cis and the trans isomers would lead to two mixtures of different dl isomers. It is not surprising that these two dl dibromides would have the same refractive index. The dibromides of the cis- and trans-2-pentenes were prepared in this laboratory and were found to have identical indices of refraction but different boiling points, densities, and freezing points. The value obtained in this laboratory for the refractive index of the dibromides, N_D^{20} 1.5096, is the same as that reported by Norris and Reuter¹⁰ but is higher than the value reported by Sherrill, N_D^{20} 1.5074 and by other investigators.

Qualitative absorption spectra measurements were reported by Dr. B.H. Carrol of the Bureau of Standards on a sample of 2-pentene supplied by Kharasch. His report is summarized in the following quotation:

"The method used permits only the statement that a shift in the limit of absorption to the longer wave lengths has been produced by exposure. This indicates an irreversible change in the composition of the sample; since applying LeChatelier's principle, and equilibrium should be shifted in the direction of decreasing absorption when the shift is due to the absorption of radiant energy."

More extended absorption spectra measurements were made by Carr. Three quotations¹² from her article follow:

"Our results show that the absorption curve for the 2-pentene prepared from 3-bromopentane differs markedly from that of the 2-pentene obtained from 2-bromopentane."

"The curves for the stable 2-pentene and trimethylethylene are almost exactly similar in form and differ only in the position of the band and to a slight degree in intensity, whereas the curve for the isomeric 2-pentene prepared from 3-bromopentane is very different. The broad step-out has disappeared entirely and there is only the slightest tendency toward an absorption band. In the longer wave lengths this isomer transmits farther; in the shorter wave lengths slightly less. The

differences are striking and of great interest in connection with the possibility of the electro-isomerism of the 2-pentenes. The shallow absorption band in this region is characteristic of all ethylenic compounds and if this absorption band is related to the second pair of electrons, the so-called labile pair, in the double bond, it would be in this band that one would expect differences in the absorption of electronic isomers to be most evident and there should be little or no difference in the second band in the far ultraviolet. In this connection it is of interest to note that in seven pairs of cis-trans isomers which have been examined by quantitative methods¹³ the two forms have very similar absorption curves, but the trans form is somewhat more absorptive and this difference becomes much more marked the shorter the wave length. It would seem, therefore, that with geometrical isomerism it is the intense band in the far ultraviolet which differs with the two isomers while in electro-isomerism it is the band of low intensity in the near ultraviolet which shows the marked differences. Although experimental data are too meager to justify far reaching conclusions, these results certainly suggest the possibility that the absorption band in the far ultraviolet is related to the characteristic frequency of the stable pair of

electrons in the double bond and these electrons are primarily concerned in cis-trans isomerism, while the second pair of electrons, being much more labile, produce the shallow band of much lower frequency and, according to the theory of Kharasch, it is the relative position of this pair of electrons which determines electronic isomerism."

"The results of the spectrographic examinations of the isomeric 2-pentenes are in accord with the interpretation of electronic isomerism as proposed by Kharasch, but are not in agreement with the previously established behavior of geometrical isomers."

The report by Dr. Carrol offers no evidence in favor of electromerism over cis-trans isomerism. The evidence offered by Carr in favor of electromerism is more difficult to evaluate. She refers to the work of Errera and Henri¹³ who measured the absorption spectra for the following eight pairs of cis-trans isomerides:

1. dichlorethylenes
2. bromethylethylenes
3. brommethylethylenes
4. chloriodoethylenes
5. maleic and fumaric acids
6. citraconic and mesaconic acids
7. crotonic and isocrotonic acids
8. crotonic and isocrotonic nitriles

In each of these cases the compounds had as substituents linked directly to the carbon atoms comprising the double bond a halogen, a carboxyl, or a nitrile group. It would seem that one must be extremely cautious in comparing these compounds with pure hydrocarbons in any discussion involving the effects of the electronic configuration or the geometrical configuration upon the absorption spectra. It is hoped that absorption spectra measurements can be taken on a series of pairs of cis-trans isomers of pure hydrocarbons in order to offer concrete evidence concerning this point.

Clark and Hallonquist¹⁴ found that 2-pentene prepared from 2-bromopentane had a slightly lower refractive index, boiling point, and density than did 2-pentene from 3-bromopentane confirming the findings of Kharasch and co-workers and of Sherrill and co-workers. Clark and Hallonquist also report values for the freezing points of the 2-pentenes. Their values are -149° for the stable form and -144° for the unstable form. The trans-2-pentene prepared in this research melted fairly sharply at -136° to -135° indicating Clark and Hallonquist's isomer was not pure. The cis-2-pentene would not crystallize but turned into a hard glass within a comparatively small temperature range, namely -180° to -178° . The melting point of the trans-2-pentene agrees with the value reported by Norris and Reuter¹⁰ $-138^{\circ} \pm 2^{\circ}$ and is higher

than all other reported values.

Clark and Hallonquist also found that neither a magnetic nor an electrostatic field had any effect upon the addition products obtained by the action of hydrogen bromide on their metastable 2-pentene. Seyer¹⁵ using samples supplied by Clark and Hallonquist made density and surface tension measurements and calculated parachors but concluded that his results were of little value in deciding whether his samples were "electromers" or cis-trans isomers.

Kharasch¹⁶ also argues that the isomeric 2-pentene samples are "electromers" rather than cis-trans isomers for the assumption of cis-trans isomerism would imply the addition of an unsymmetrical reagent (hydrogen bromide) in a different manner to the two different isomers. However, when one considers that the isomeric 2-pentenes have different degrees of symmetry and that both forms are unsymmetrical, it is not to be expected that an unsymmetrical reagent would add in the same manner to each. Kharasch in his earliest article¹⁶ stated that he was studying the oxidation of the "electromers" with permanganate in an effort to determine whether they were cis-trans isomers. No report of this investigation could be found in the literature.

The only direct experimental evidence in favor of "electromeric isomerism" over cis-trans geometrical isomerism was the refractive index of the 2,3-dibromopentanes

obtained by Sherrill. It has been shown that both *cis*- and *trans*-2-pentene give different dibromides with identical indices of refraction. It has been pointed out that the evidence from the absorption spectra and from the addition of hydrogen bromide to 2-pentene in no wise contradicts the statement that the unstable or metastable 2-pentene is merely *cis*-2-pentene and that the stable isomer is *trans*-2-pentene.

The above discussion has been limited strictly to the nature of the evidence offered by the supporters of "electromerism" and might well be amplified by the statement that the isolation of two isomeric substances, differing solely in the position of one of the electron pairs is impossible according to our knowledge of the structure of molecules.

We believe that the concept of "electromeric isomerism" as advanced by Kharasch is unsupported by experimental evidence and is untenable according to modern structural chemistry.

EXPERIMENTAL

α - Hydroxy - α - Methylvaleric Acid.

This acid was obtained through the cyanhydrin synthesis from 2-pentenone, B.P. 102.0-102.1° at 757 to 759 mm. which was kindly furnished by the Standard Oil Development Company. In a 3-necked, 3-liter flask equipped

with a mechanical stirrer, a thermometer, and a dropping funnel and surrounded by a freezing bath were placed 516 g (6.0 mole) of 2-pentanone and 330 g (6.3 mole) of sodium cyanide (96-98%, powder form). To 500 g. of ice was added 540 g (6.0 mole) of C.P. concentrated nitric acid (Sp.G. 1.42) and the resulting cold solution allowed to flow into the ketone-cyanide mixture during vigorous stirring keeping the temperature below 20° until near the end when the temperature was allowed to rise to 25°. This addition required from 40 minutes to 1 hour. The amount of water used was just sufficient to hold in solution at 25° the sodium nitrate formed in the reaction. Since its molal solubility in water is the highest of the common salts, its saturated solution had the least tendency to dissolve the cyanhydrin. The crude cyanhydrin layer was separated and immediately mixed with 800 ml. (8.mole) of C.P. concentrated hydrochloric acid (Sp.G. 1.19) in a flask provided with a reflux condenser. The mixture warmed spontaneously and the heat of reaction was sufficient to keep the flask contents boiling for a couple of hours. The refluxing was continued, by applying a flame, for a total of eight hours. The mixture was allowed to cool, 300 g. of water and 150 g. of anhydrous sodium sulfate was added and the mixture shaken. This sodium sulfate treatment removed considerable HCl. The oil phase was separated and the aqueous phase was extracted with 2- 300 ml. and 1-150 ml. portion of ethyl ether. The

combined oil phase and ether extracts were treated (in three portions) with 100 g. sodium sulfate dissolved in 350 g. water, and then dried over anhydrous sodium sulfate. When dry the extract was placed in a still carrying a 20 cm bead column and equipped with a very wide (20 mm.) side arm. The ether was removed at ordinary pressure and the ketone removed by use of an aspirator. About 100 g. of crude ketone was recovered. The pressure was then lowered and the hydroxyacid distilled. The overall yield was 60-65%, based on the amount of ketone used up - 75 - 77%, of a product of B.P. 85° to 91° at 0.6 to 1.0 mm. and M.P. 49-51°. When crystallized from toluene the acid melted at 54.-54.5°. Equivalent weight crude product 133.4 by titration (theory 132.1).

Cis- and trans- α - methyl- β -ethylacrylic Acid.

A mixture of these two isomeric acids along with some lactide was formed by the decomposition of the alpha-hydroxy-alpha-methyl valeric acid by heating about 250 g. in a 500 ml. flask carrying a thermometer and a 15 cm. column of glass rings. The column was 2.5 cm. in diameter and had a 1.2 cm. side arm. The heating was regulated so that about 20 minutes were required to bring the temperature of the distillate up to 200°, the receiver changed and the remainder distilled over in about 30 minutes. At this rate a yield of the crude acid of 85-90%, containing some unchanged hydroxy acid, was obtained. Heating at a slower rate caused the formation of more lactide and at a faster rate caused more

unchanged hydroxy acid to distill over. The cis-trans mixture was fractionated three times through a 50 x 3.0 cm. column of glass rings at 10 mm. pressure. The result was in two fractions: cis- B.P. 94.4° at 10 mm. $N_D^{25} = 1.4480$, M.P. - 42.° and trans, B.P. 106.5 at 10 mm., $N_D^{25} 1.4570$, and, when recrystallized from 50% aqueous methanol, M.P. 24.1°. This agrees with the M.P. given by von Lang¹⁷. The yields were 30% of cis- and 20% of trans-. The trans acid was all recrystallized from 50% aqueous methanol before use. Unsuccessful attempts were made to recrystallize the cis- form from various solvents. In the course of these attempts it was noticed that this cis- form apparently would crystallize as the mono-hydrate when a solution of equimolar amounts of the acid and water dissolved in methanol was cooled in a solid CO₂- alcohol bath. This hydrate was not investigated further.

Some p-phenylphenacyl bromide was synthesized according to the method of Drake and Bronitsky¹⁸ and the p-phenylphenacyl esters of the two isomers were made. After purification they melted as follows:

cis ester 44.5 - 45.5°

trans ester 90-91°

The dibromides of the two acids were made in carbontetrachloride solution. Upon removal of the solvent the dibromide from the trans acid crystallized while that from the cis remained an oil which slowly crystallized yielding the same dibromide as the trans acid as shown by

mixed melting points. The dibromide melted at 97-98°. This is in agreement with von Lang²⁰ who found that this method yielded only the dibromide of the trans acid M.P. 97.6°.

To check on the presence of α -propyl acrylic acid which might have been formed during the dehydration of the hydroxy acid, samples were ozonized following the method of Church, Whitmore and McGrew¹⁹. This method led to a 60% recovery of propionic aldehyde with no indication of formaldehyde being present. As this ozonization was done both on an intermediate (about 50-50 cis-trans) fraction, and on a pure trans fraction, M.P. 24.1° and as propionaldehyde was the only volatile aldehyde isolated it indicated that the desired isomers were the only ones present, as other unsaturated acids would not lead to the formation of propionaldehyde.

The residues from the decomposition of the hydroxy acid and from the fractionation of the unsaturated acids were combined and fractionated. The distillate, very probably the lactide, had a B.P. 82.5 - 84.3° at 0.4 mm. and n_D^{25} 1.4475. The yield of the lactide was about 20%.

The Hydriodides of α Methyl β Ethylacrylic Acid.

The addition of hydrogen iodide to the unsaturated acids was carried out according to the general method of Talbot³ as modified by Young, Dillon, and Lucas⁴.

An anhydrous solution of hydrogen iodide (0.6-0.7N) in chloroform was made by passing pure, anhydrous hydrogen iodide²¹ into 700 ml dry chloroform contained in a 2-liter

pyrex distilling flask provided with a ground glass stopper carrying an inlet tube reaching nearly to the bottom. The chloroform was kept at -15° and the side arm, which constituted the outlet tube, was provided with a drying tube of phosphorous pentoxide. The concentration of hydrogen iodide was determined at intervals by titrating 2.00 ml. portion against 0.134 N NaOH. As soon as the required amount of hydrogen iodide was in solution - (0.52 to 0.62 moles), the unsaturated acid (0.33 moles dissolved in chloroform) and a few grams of molecular silver, to remove any iodine formed, were quickly added. The outlet tube of the flask containing the reactants was sealed off, the ground glass stopper wired in, and the flask placed in the dark in a refrigerator for 10 to 13 days. It was then cooled to -15° , the side arm opened, the inlet tube removed and a capillary inserted in its place. The flask was then pumped off at 20 mm. on the aspirator till the excess hydrogen iodide was removed and then at $1/2$ to 1 mm. until all of the chloroform was removed. Appropriate traps, and drying tubes were used to prevent water vapor from entering the flask and to protect the pump. During this process the evaporation of the chloroform cooled the flask to considerably below 0° , estimated to be at least as low as -20° . After the chloroform was all removed, as evidenced by the warming up of the flask and by the absence of any distillate, the pumping was continued for about three

hours while the flask was at room temperature. In the case of the hydriodide from the cis acid the product would not crystallize from any of the solvents tried. There was thus the possibility of some of the hydriodide of the stable form being present, formed by rearrangement during the addition of the hydriodic acid and subsequent treatment. To minimize this danger of the rearrangement the additions and all work connected with the hydriodide was conducted in a room from which sunlight was completely excluded, the hydriodide was always kept at 3° or lower except for the last three hours of the distillation process, iodine was excluded as much as possible, and the hydriodide was decomposed immediately after it was isolated. All of the above agencies are known to slow down or stop rearrangements of this type. In the case of the trans acid, the hydriodide crystallized out on removal of the chloroform. The crude acid melted at 38.5 to 41.5° while the recrystallized acid melted at 42.0 to 42.3°.

The ratio of hydrogen iodide to unsaturated acid was thus always kept greater than 1.5. The anhydrous chloroform used was purified by washing with 40% sulfuric acid, water, drying over calcium chloride, and distilling through a long column of glass rings. The first fraction, containing moisture from the apparatus, was discarded.

The molecular silver was prepared by electrolytic reduction of freshly precipitated silver chloride. This was accomplished by leading a platinum wire from the silver chloride to a zinc anode in a porous cup, the whole immersed in a large beaker of dilute hydrochloric acid. This process required several days but yielded, upon washing and drying over phosphorous pentoxide, a very pure product uncontaminated by organic material. It was found that silver prepared by the reduction of silver ion by use of sugar or formaldehyde would catalyze the decomposition of the hydrogen iodide due to adsorbed organic material which could not be completely removed.

The Isomeric 2-Pentenes.

The pentenes were generated in a 3-necked, 2-liter flask provided with a mechanical stirrer, thermometer and an outlet tube. To the latter was attached in series a spiral wash bottle of aqueous 20% sodium hydroxide solution heated in a water bath to 45°, and an ice water condenser leading into a trap immersed in ice. The outlet of the trap was connected to a reflux condenser cooled with solid carbon dioxide. The hydriodide from 0.33 moles of the unsaturated acid and 28.6 g. sodium carbonate dissolved in 650 ml. ice water were added to the reaction flask, stirring started, and the mixture allowed to warm up. Immediately a gas was evolved which was not completely absorbed in the wash bottle. The mixture was warmed with a flame until after about one and one half hours the mixture

was boiling. In the case of the cis- isomer* practically all the pentene had distilled over by the time the reaction temperature reached 60°. The trans- isomer was mostly all generated by the time 40° was reached. There was no marked separation of the gas evolution into stages of pure carbon dioxide or pure pentene evolution as was noticed in the case of the butenes²². The yield was 50-55% with the cis- and 85 - 90% in the case of the trans- isomer. The hydrocarbons were dried over calcium chloride and slowly distilled through a fractionating column consisting of 4.5 meters of 5 mm. I. D. pyrex tubing wound in 25 coils. In each case the middle or main fraction was then refractionated. Refractive indices taken on all fractions and residues showed the second fractionation to effect no further change in composition. The residues from the first distillation gave faint tests for chloroform when treated with aniline and alkalie solution. It is significant, however, that the chloroform was practically all removed in the first distillation as shown by refractive indices. The results of these distillations are given in Tables I and II for the cis and trans isomers respectively. The refractive index of chloroform is included for convenience.

*By analogy to the preparation of the isomeric 2-butenes^{3,4} the hydrocarbon from the low melting low boiling unsaturated acid was considered to be the cis-form and from the high melting high boiling acid the trans-.

TABLE I (cis)

Distillation	I		2		CHCl ₃
Fraction	Distillate	Residue	Distillate	Residue	
Wt. g.	22.	4.	16.	6.	
B. P.	35.5° 742 mm		35.4° 739.5 mm		
Reflux Ratio	12:1		10:1		
n_D^{20}	1.3812	1.3900	1.3811	1.3816	1.4462

TABLE II (trans)

Distillation	1			2 (Redistillation Fraction No.1)	CHCl ₃	
Fraction	1	2	Residue	Distillate	Residue	
Wt. g.	20.5	28.5	4.5	15.5	3.5	
B. P.	35.4° 739 mm	35.4° 739 mm	-	35.4° 740 mm	-	
Reflux Ratio	6:1	6:1		7:1		
n_D^{20}	1.3795	1.3795	1.3858	1.3794	1.3795	1.4462

The trans form prepared here is believed to be very pure from its synthesis and from its high melting point. The cis form may be contaminated with some of the trans isomer as the hydriodide of the unsaturated acid could not be crystallized. However, the synthesis was done under conditions which led to as pure a product as possible. It is significant that the difference in refractive indices is greater for the pentenes prepared here than for the pentenes reported by Sherrill and co-workers.

Table III contains the physical properties of the 2-pentenes as determined in this laboratory as well as some values of other investigators for comparison.

TABLE III

Compound	Boiling Point		n_D^{20}	F. P.	Source
	740 mm	760 mm			
Cis-2-pentene	35.4	36.2 †	1.3817	(-180-178°)*	This Laboratory
Trans-2-pentene	35.4	36.2 †	1.3799	-136-5°	This Laboratory
Trans-2-pentene	35.7		1.3797		Lauer and Stodola
2-pentene from sec-amyl alcohol		36.4	1.3808	-138° 2°	Norris and Reuter
2-pentene from diethyl carbinol		36.4	1.3817 @ 17.2°	-147°	VanRisseghem
Pentene from 3-bromopentane		36.30	1.37965		Sherrill
Pentene from 2-bromopentane		35.35	1.37849		Sherrill
Meta-stable 2-pentene		36.5	1.37960	-144°	Clark and Hallonquist
Stable 2-pentene		35.8 755 mm	1.37845	-149°	Clark and Hallonquist

*Vitrification Point, would not crystallize

†Calculated.

Our trans- 2-pentene agrees in properties with that prepared by Lauer and Stodola and with the sample prepared by Norris and Reuter which was probably largely the trans- form. The refractive indices of our samples are somewhat higher than those reported by Sherrill and by Clark and Hallonquist. The freezing points indicate that Clark and Hallonquist's samples were impure.

The Isomeric 2,3-Dibromopentanes.

These were prepared by slowly dropping liquid bromine in an all glass apparatus onto the liquid pentene well agitated and cooled in an ice-hydrochloric acid bath and kept in the dark. This procedure was adopted because it led to a product uncontaminated with a solvent or with substitution products. At no time during the process was there any excess bromine present except during the instant the bromine drops hit the swirling mixture. The bromine used was purified by treatment with concentrated aqueous potassium bromide solution followed by washing, drying, and distilling from concentrated sulfuric acid. Immediately after the bromination the crude product was quickly washed with dilute sodium bisulphite solution, twice with sodium bicarbonate solution, four times with water and then dried over calcium chloride. The dried product was distilled through a Weston column²³ maintaining a reflux ratio of forty to one. Redistillation of the main fraction showed no change in refractive index or boiling point. The physical properties are given in Table IV along with some values of other investigators.

TABLE IV

Substance	B.P.	N_D^{20}	d_4^{20}	F.P.	Source
dibromide from cis- 2-pentene	92.4° 50.1 mm	1.5096	1.6817	-44 to -41°	This Laboratory
dibromide from trans- 2-pentene	91.0° 50.1 mm	1.5096	1.6809	-55 to -53°	This Laboratory
dibromide from 2-pentene	180.2-80.5° 760 mm	1.5098			Norris and Reuter
dibromide from 2-pentene	60.5-61° 14 mm	1.5093 @ 17°		-66°	VanRisseghem
2,3- dibromo- pentane	178-179° 760 mm	1.5074			Sherrill

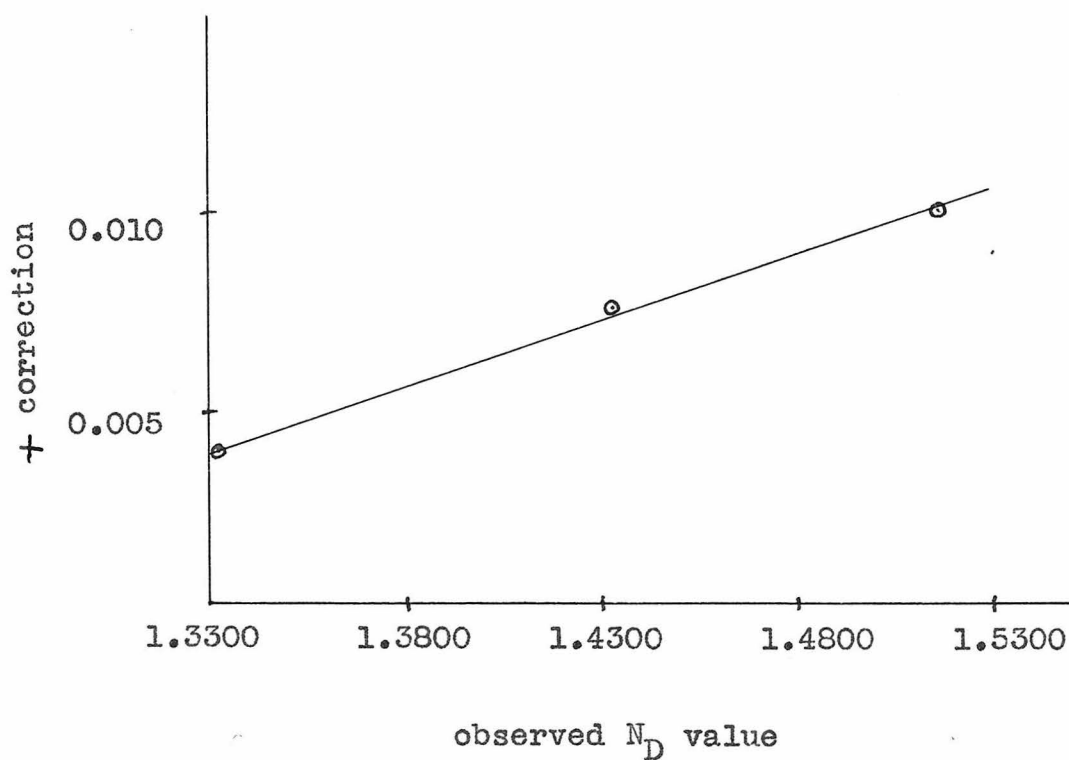
While the value of the refractive index obtained in this research is higher than that obtained by Sherrill, it is significant that both the cis- and the trans- 2-pentene yielded dibromides having the same refractive index but differing in other physical properties. It was due to this identity of refractive indices that the erroneous assumption was made that the 2-pentene samples all yielded the same dibromide.

Refractive Indices

The refractive indices were determined by use of a Zeiss Abbe refractometer. It was calibrated against conductivity water, N_D^{20} 1.33299, and two standard prism

test plates.

N_D 1.44338, and N_D 1.5175. The corrections were found to lie on a straight line and all values recorded in this paper were corrected by the corresponding value obtained from the curve. The curve is reproduced below:



SUMMARY

The pure isomeric cis- and trans- 2-pentenes have been synthesized from the pure cis- and trans α -methyl- β -ethylacrylic acids. The corresponding dibromopentanes have been made. The isomeric 2-pentenes were found to have identical boiling points but refractive indices differing by a larger amount than previously reported values. The freezing point of the trans form is higher than any previously reported value. The dibromides from these pentenes were found to have identical indices of refraction but different boiling points, freezing points, and densities. The freezing points were found to be higher than previously reported values. It has been shown that it is incorrect to assume because of the refractive index that only one dibromopentane is obtained from the 2-pentenes and thus that there is no direct experimental evidence in favor of the concept of "electromeric isomerism" in contradiction to the older more general concept of cis-trans isomerism. It was pointed out that "electromeric isomerism" is in contradiction to modern views of molecular structure.

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THE REACTION BETWEEN OXYGEN AND 2-BUTENE

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The Reaction between Oxygen and 2-Butene

By H. J. LUCAS, A. N. PRATER AND R. E. MORRIS

Introduction

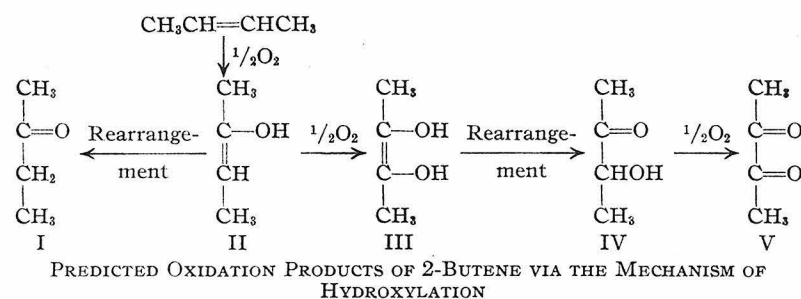
Early in his investigations of the autoxidation of hydrocarbons Bone extended his hydroxylation theory to include unsaturated hydrocarbons.¹ He contended that the first step in the reaction between oxygen and ethene was the formation of vinyl alcohol, since acetaldehyde was isolated as a reaction product. Bone² 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.

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 re-

- (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.

agent 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 dimethylglyoxal⁵ 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

(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.

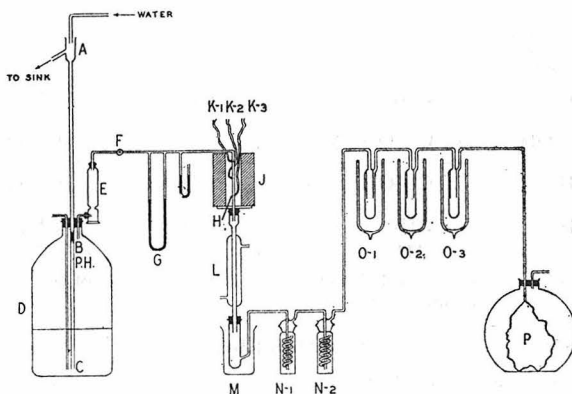


Fig. 1.

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 oxide⁸ 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, $\text{HOCH}_2\text{OOCH}_2\text{OH}$. However, a peroxide and an aldehyde alone could account for this change, since an aqueous solution of hydrogen peroxide, formaldehyde and sulfuric acid⁹ or one of hydrogen peroxide, paraldehyde and sulfuric acid¹⁰ 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

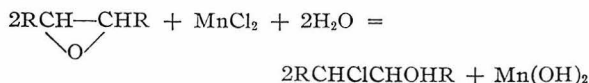
(7) Weston, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

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

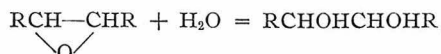
(9) Fry and Payne, *THIS JOURNAL*, **53**, 1973 (1931).

(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



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 oxide¹¹



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 Brady¹³ 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 alumina¹⁴ 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

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

(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).

TABLE I
ANALYSIS OF GASES

Temp., °C.	Av. rate of flow, cc./min.	Entering gas			C ₄ H ₈ , Moles	Exhaust gas, %							
		C ₄ H ₈ , %	O ₂ , %	N ₂ , %		CO ₂	O ₂	N ₂	CH ₄	CO	H ₂	C ₄ H ₈	
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 C₂ and C₃ hydrocarbons absent, some C₄ present.

TABLE II
ANALYSIS OF CONDENSABLE PRODUCTS

Temp., °C.	C ₄ H ₈ Br ₂		C ₄ H ₈ Br ₄		Ice-trap condensate		2,4-Dinitrophenylhydrazones		Acid equiva- lents	Per- oxide	Olefin oxide	
	G.	Mole	G.	Mole	Water, ml.	Oil, ml.	Mol. wt.	Moles as CH ₃ CHO				(CHO) ₂ %
375	66.5	0.308	1	0.003	0.00464	Trace	+	-	+
415	51.6	.239	1.4	.0038	0.10127	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 ₄ H ₈			C ₄ H ₆	C ₈ H ₁₆ crude	Aldehydes		Acid	CO	CO ₂	H ₂	CH ₄
	C ₄ H ₈ Br ₂	Exit gas	reacted			CH ₃ CHO	(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

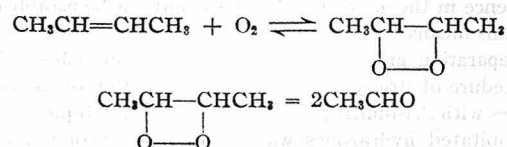
^a Estimated.

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 peroxide¹⁵ and the decomposition of this into two molecules of acetaldehyde



Using the bond energies of Pauling¹⁶ 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

(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 monoxide²³ 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 Lenher³ for ethene. However, this does not seem to be important except at the highest temperatures, where the mechanism was more complicated.

(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).

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

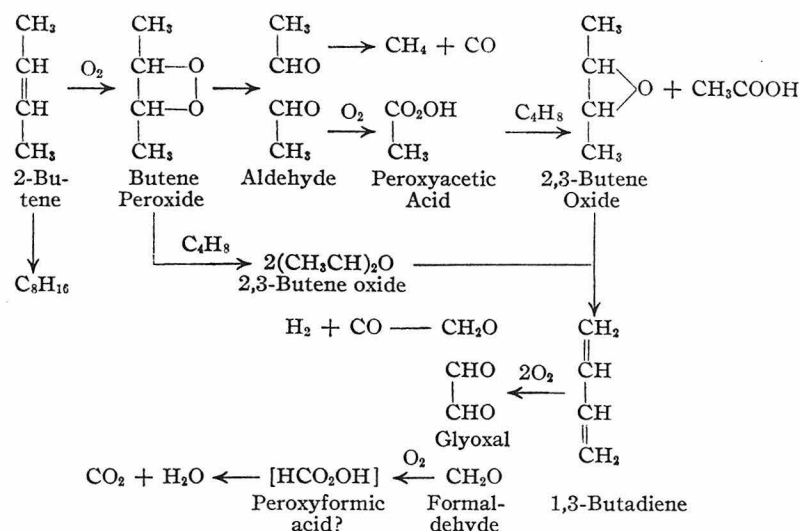


Fig. 2.—Mechanism of 2-butene-oxygen reaction.

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.

PASADENA, CALIF.

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