for the most part a powder, the particles of which are individual crystallites or groups of them with sufficiently small intercrystallite cracks as to be undetectable under the conditions of a particular experiment. On this basis one would expect a linear rise of pressure as water molecules filled more and more forbidden sites in the crystallites of small granules. The same process would be expected of a larger granule but the effect would be obscured by superimposition of another effect due to the tendency of intercrystallite pore walls to act something like solid surfaces. This explanation leaves the apparent hysteresis to be associated with the properties of the dihydrate. The latter seems plausible in the light of a statement by Kelley (*12*) that β-hemihydrate "probably does not exist as such in the presence of H_2O (*l*) or in the presence of the implied equilibrium pressure of H_2O (*g*)."

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Catalytic Vapor-Phase Oxidation of Some Four-Carbon Hydrocarbons

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ALTHOUGH the catalytic vapor-phase oxidation of hydrocarbons, using air as the oxidizing agent, is quite attractive economically, relatively few hydrocarbons have been oxidized successfully in this manner on a commercial scale. The oxidation of naphthalene and *o*-xylene to phthalic anhydride, benzene to maleic acid, and ethylene to ethylene oxide may be cited as typical examples of successful industrial applications. Associated with the above process are such problems as heat removal at relatively high temperature levels, temperature control, and recovery of product from a gas stream diluted by the large excess of air usually required. These problems must be solved if the process is to be successful. Of equal importance in determining whether or not a hydrocarbon may be processed successfully in the above manner are such chemical factors as the stability of the product toward further oxidation and the thermal stability of both hydrocarbon and product. All of the above factors are influenced by the specific or nonspecific nature of the catalyst employed.

With the view of extending the range of application of the above process, it would be extremely desirable to have quantitative information on the effect of hydrocarbon structure, catalyst type and structure, and operating conditions on the types and amounts of products formed. In addition, it would be desirable to have information on the behavior of the intermediate products themselves when subjected to conditions similar to those used for the hydrocarbons. From such information as that outlined above, at least for a particular catalyst, it might be possible to formulate a scheme of oxidation from which results for other hydrocarbons can be predicted. With this point of view in mind, it is evident that the information supplied by any experimental investigation must necessarily be complete in regards to both the qualitative analysis and identification of products, and to the quantitative determination of each of these products in the presence of the others. Very often investigators in this field have circumvented the analytical difficulties by reporting only products occurring in preponderate amounts and promising to be of special interest. In the present investigation, however, efforts were made to identify all constituents in the product and to develop satisfactory recovery and analytical procedures for quantitative determination. Such procedures are believed to be valuable to anyone engaged in similar research and therefore are described in this paper.

The purpose of the present investigation is to furnish information such as that outlined above for several four-carbon hydrocarbons over a few selected catalysts. The hydrocarbons selected for study were *n*-butane, 1-butene, 2-butene, isobutylene, and 1,3-butadiene.

Several silver and silver oxide catalysts and one vanadium pentoxide catalyst have been studied in this investigation. Silver and silver oxide catalysts have been successfully used in the oxidation of ethylene to ethylene oxide and it was thought that such catalysts might prove to be effective in the oxidation of the four-carbon olefins. Vanadium pentoxide is an effective catalyst for a large number of oxidation processes and this was the basis for its selection.

The major portion of this investigation represents a study of the vapor-phase oxidation of isobutylene, 1-butene, 2-butene, and butadiene over the silver, silver oxide, and vanadium pentoxide catalysts. Butane proved to be quite resistant to oxidation and for this reason only a few runs were made with this hydrocarbon. Mainly for the purpose of checking equipment performance and catalyst activity, the oxidation of ethylene over a silver oxide catalyst was also investigated. In addition to the above, a few qualitative runs using vanadium pentoxide as a catalyst were made with acetaldehyde, formaldehyde, carbon monoxide, and hydrogen in the hope that information obtained therefrom might be of use in probing into the mechanism of the hydrocarbon oxidation.

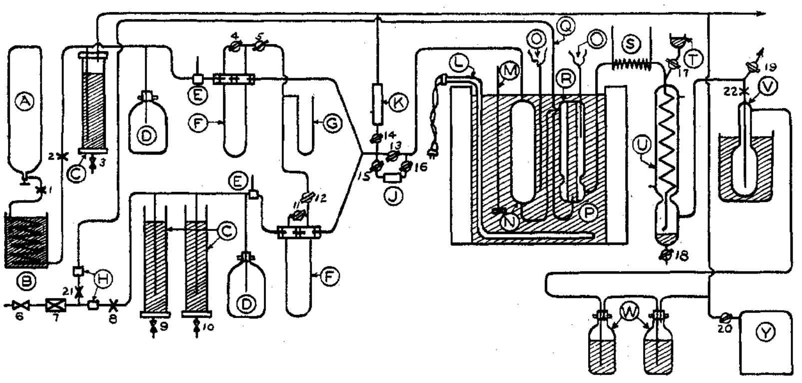


Figure 1. Flow Diagram

A. **Hydrocarbon cylinder**
B. **Hydrocarbon vaporizer**
C. **Pressure regulators**
D. **Surge tanks**
E. **Thermometers**
F. **Flowmeters**
G. **Manometer**
H. **Oil filters**
J. **Gas sampler**
K. **Capillary tube**
L. **Immersion heater**
M. **Stirrer**
N. **Preheater**
O. **Thermocouples**
P. **Salt bath**
Q. **Air jet line**
R. **Reactor**
S. **Heater**
T. **Flushing attachment to *U***
U. **Primary condenser**
V. **Cold trap**
W. **Scrubbers**
Y. **Gas analysis equipment**

The operating conditions which were varied in this investigation were temperature, air-hydrocarbon ratio, and contact time. All runs were made at substantially atmospheric pressure.

PREVIOUS INVESTIGATIONS

Because of the extent of the general field of hydrocarbon oxidation, only those references which have a direct bearing on the present investigation are cited. For further information the reader is referred to the text by Marek and Hahn (*13*) and recent summary papers by Egloff, Nordman, and Van Arsdell (*5*) and Rust and Vaughan (*16*).

References to the use of solid catalysts in effecting the vapor-phase oxidation of the four-carbon hydrocarbons are few and are to be found only in the patent literature. Vanadium and/or molybdenum compounds have been used as catalysts for the oxidation of 1-butene, 2-butene, and butadiene to maleic acid at atmospheric pressure using a large excess of air (*22*). Under these conditions and at a temperature of 350° C., the yields (based on hydrocarbon reacted) of maleic acid from 1-butene, 2-butene, and butadiene were 24, 23, and 28%, respectively, of the theoretical values. It has been claimed (*18*) that admixing steam with the air and hydrocarbon results in higher yields of maleic acid when the above conditions and catalysts are used. Thus, the yield of maleic acid from butadiene was increased from 31 to 40.6% by the admixture of steam under otherwise similar conditions. Molybdenum oxide has been used as a catalyst for the oxidation of *n*-butane (*10*). A mixture of aldehydes and acids resulted. Good yields of α-methylacrolein from isobutylene, crotonaldehyde from 2-butene, and methyl vinyl ketone from 1-butene have been claimed with metal selenites and tellurites as catalysts (*2*). A 30% conversion (based on hydrocarbon entering) of isobutylene to α-methylacrolein was obtained at 230° C. The activities of these catalysts decreased rapidly with use and frequent regeneration with air or air containing small amounts of nitrogen oxides was necessary. Cuprous oxide has also been used as a catalyst for the oxidation of the four-carbon olefins (*8*)—e.g., methyl vinyl ketone being obtained from both 1-butene and 2-butene. Catalysts containing silver or silver compounds have been claimed as suitable for the oxidation of olefins to olefin oxides, although ethylene was the only olefin for which experimental data were given.

MATERIALS

Technical grade hydrocarbons supplied by the Phillips Petroleum Co. were used in this investigation. The minimum purities as reported by the manufacturer were 99 mole % for butadiene and *n*-butane and 95 mole % for 1-butene, 2-butene, and isobutylene. The 2-butene was a mixture of the cis and trans forms.

APPARATUS

A diagrammatic flow sheet for the apparatus used in this investigation is shown in Figure 1.

The hydrocarbon to be oxidized passes from the hydrocarbon feed cylinder, *A*, where it is in a liquid state, through needle valve, *1*, to vaporizer, *B*, which is heated with open steam. The gaseous hydrocarbon, slightly preheated, then passes through needle valve, *2*, to the hydrocarbon pressure regulator, *C*. A small amount of hydrocarbon bubbles continuously out of the regulator and is removed from the system through a vent line. The water level in this regulator determines the pressure causing flow. Leaving the pressure regulator the hydrocarbon passes through surge tank, *D*, and orifice flowmeter, *F*. A thermometer, *E*, is placed in the line just preceding the flowmeter and a static pressure manometer, *G*, is connected to the downstream side of the flowmeter. Low pressure air from the laboratory supply passes through gate valve, *6*, diaphragm reducing valve, *7*, oil filter, *H*, and needle valve, *8*, to two pressure regulators, *C*, similar to the one used in the hydrocarbon inlet line. A surge tank, *D*, orifice flowmeter, *F*, and thermometer, *E*, are also included in the inlet air line, and the static manometer, *G*, is also connected to the downstream side of the air flowmeter. After passing through the flowmeters, the hydrocarbon and air are mixed and the gaseous mixture can then pass through the reaction system proper or, by suitable manipulation of stopcocks *13* and *14*, be diverted to the vent line through the capillary tube, *K*. This capillary simulates the pressure drop through the reaction system and permits regulation of flow rates and air-hydrocarbon ratios previous to passing the gases through the reaction system. When stopcock *14* is closed and *13* is opened, the gaseous mixture passes through the preheater, *N*, and reactor, *R*, and then the product mixture passes out to the recovery system. Preheater *N* and reactor *R* are immersed in a molten salt bath, *P*, which is heated by an electrical immersion heater, *L*. An inlet gas sampler, *J*, is provided for checking inlet gas compositions. The exit gases from the reactor are kept hot by an electrical heater, *S*, to prevent solid product deposition in the line preceding the primary condenser. The main body of the molten salt is agitated by stirrer, *M*, while agitation in the central bore of the reactor, *R*, is effected by an air jet, the air being supplied from the inlet line through needle valve *21* and oil filter, *H*. The air jet line is designated as *Q* in Figure 1. Thermocouples, *O*, are provided for the measurement of bath and catalyst-bed temperatures.

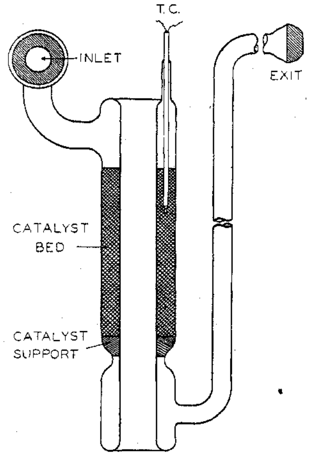


Figure 2. Reactor

The product gases leaving the reactor are first cooled in the primary condenser, *U*, which has cooling water flowing through the jacket. This condenser may be cleaned prior to a run by rinsing with water through attachment, *T*. The gases from the primary condenser can pass through either of two recovery trains by suitable manipulation of stopcocks *19* and *22*. One of these trains is usually used for the pre-run, while the other is reserved for the quantitative run. The recovery trains used in this investigation are described in detail below. In general, one or more cold traps, such as *V*, and several scrubbers or absorbers, such as *W*, are used. A gas analysis equipment, *Y*, is installed at the end of the recovery train and samples of the exit gas are drawn directly into the apparatus for analysis.

The reactor, shown in Figure 2, is 20 cm. in length, exclusive of the entering and exit lines; its outside diameter is 4 cm. and the diameter of the central bore 2 cm. The entering line is made larger than the exit line to facilitate catalyst removal. The catalyst is placed in the annular space and is supported on glass beads. The position of the thermocouple is indicated in Figure 2.

The apparatus as shown in Figure 1 was that used for the oxidation of the four-carbon hydrocarbons. Slight modifications not indicated in Figure 1 were made in the equipment for the runs with ethylene, hydrogen, carbon monoxide, formaldehyde, and acetaldehyde.

OPERATIONAL PROCEDURE

Before any quantitative runs could be made for a given catalyst, it was necessary to establish the identity of the products formed in the reaction. For this purpose several preliminary runs covering moderate ranges of contact time, temperature, and air-hydrocarbon ratio were made and a qualitative analysis was carried out on the various condensates and solutions in the recovery train. From the results of this analysis, quantitative analytical procedures and a suitable recovery train were decided upon for the quantitative runs. If no intermediate products were found, more runs were made over a wider range of variables and in addition to the qualitative analysis of the solutions in the recovery train, a quantitative analysis of the exit gas was carried out. Before it was accepted that no intermediate products were present, two conditions had to be satisfied—the carbon entering the system in the form of hydrocarbon must be equal to the carbon leaving the system in the form of unreacted hydrocarbon, carbon dioxide, and carbon monoxide, and the results of the qualitative analysis must be negative. Runs in which intermediate oxidation products were present and for which quantitative data were to be obtained actually consisted of two parts—the pre-run and the quantitative part of the run. The pre-run represented the time required to set up a steady state. During this pre-run various readings were taken and exit gas analyses made periodically. A steady-state condition was indicated by constant catalyst-bed temperature and exit gas composition. At the end of the pre-run the primary condenser was drained, flushed several times with warm water, and the recovery trains were switched. During the quantitative part of the run readings were taken periodically and as many exit gas analyses made as time permitted.

In the first few runs of a series made with a given catalyst the location of the thermocouple in the catalyst bed was varied to find the position of maximum temperature. After this position had been located, the remaining runs were made with the thermocouple fixed there. It was established that the position of the maximum temperature was essentially a function of flow rate only, and for this reason the total flow rate was held approximately constant for a given series of runs, the contact time being changed by changing the amount of catalyst.

In the majority of the runs the total bed volume was kept essentially constant by adding inert material such as glass beads or carrier alone to compensate for any active catalyst removed. Glass beads usually served as the support for the catalyst bed. For very short contact times the small amount of catalyst involved was stratified between thicker layers of inert carrier of the same mesh size.

CATALYSTS

The basic types of catalysts used in this investigation, their methods of preparation and physical characteristics, are given below.

SILVER OXIDE–BARIUM PEROXIDE ON ACTIVATED ALUMINA. This catalyst was prepared using the procedure of McBee, Hass, and Wiseman (*11*). It was of 20- to 30-mesh size, contained 52% voids, and was a brown-black color when fresh, and gray after being used.

SILVER FROM THERMAL DECOMPOSITION OF SILVER OXALATE. This catalyst was prepared using the procedure of Ryerson and Oppenheimer (*17*). It consisted of gray-colored, irregular spongy particles of various sizes and contained 93.5% voids.

SILVER OXIDE–BARIUM PEROXIDE ON ALFRAX. The procedure used for preparing this catalyst is given in (*11*). The catalyst had a mesh size of 10 to 14, contained 61% voids, and was a brown-black color when fresh, gray after use.

FINELY DIVIDED SILVER ON ACTIVATED ALUMINA. Ninety grams of silver nitrate were dissolved in 300 ml. of distilled water and 200 grams of activated alumina were added. This mixture was allowed to stand for 10 minutes to permit the alumina to become saturated with the solution. One hundred ml. of a 1 to 1 mixture of concentrated ammonium hydroxide and water were then added, and commercial formalin solution was added drop by drop with vigorous agitation until precipitation ceased. The solid material was permitted to settle and the clear solution decanted. This process of settling and decanting was repeated until the precipitate was thoroughly washed (about 6 times). The remaining slurry was stirred vigorously and evaporated slowly. After evaporating nearly to dryness, the pastelike mixture was placed in a porcelain dish and dried in an oven for 10 hours at 125° C. After drying, the catalyst mass was broken and the fines were removed by screening. A small catalyst granule was broken and the center was found to be black, indicating that the carrier was completely impregnated with the silver.

This catalyst had a black color when fresh and became gray after being used, contained 57.6% voids, and had a mesh size of 10 to 14.

VANADIUM PENTOXIDE ON ALFRAX. Twenty-five grams of powdered vanadium pentoxide were dissolved in an aqueous sodium hydroxide solution containing an excess of sodium hydroxide. It was necessary to boil the solution to dissolve the greater portion of the vanadium pentoxide. The solution was filtered hot with filter aid, the filtrate having a deep red color. This filtrate was neutralized to litmus with hydrochloric acid and allowed to stand overnight. To obtain the vanadate form, which has a yellow color, it was necessary to add 100 ml. of hydrogen peroxide (commercial solution) and 10 ml. of 5% sodium hydroxide and to boil this final mixture. Forty grams of ammonium chloride were then added and the solution was allowed to cool. Ammonium metavanadate precipitated out of solution and was filtered on a Buchner funnel and washed with 800 ml. of ammonium chloride solution. One hundred grams of Alfrax, washed successively with cold and hot water, were added to a beaker along with water and the ammonium metavanadate. The solution was evaporated, with constant stirring, and finally dried overnight in an oven at 100° C.

This vanadium-type catalyst was given a further pretreatment before use by passing a 2% by volume mixture of butadiene in air over the catalyst bed for about 5 hours at 250° C. Ammonia was given off and the yellow color changed to blue-black.

This catalyst was of 10- to 14-mesh size, contained 63.2% voids, and was a blue-black color.

RECOVERY, IDENTIFICATION, AND QUANTITATIVE DETERMINATION OF PRODUCTS

RECOVERY. In general, the recovery system for the runs with the four-carbon hydrocarbons consisted of arrangements of several or all of the recovery units shown in Figure 3.

The primary condenser was a spiral-type, borosilicate glass condenser fitted at the lower end with a condensate trap and at the upper end with a flushing attachment. The scrubbers were 125-ml. glass bottles with sintered-glass or perforated-bulb gas dispersers. The ice and dry-ice traps were of conventional design and require no description other than that given by Figure 3. Each hydrazine scrubber contained approximately 75 ml. of a saturated solution of 2,4-dinitrophenylhydrazine (2,4-DNPH) in 2 *N* hydrochloric acid. The methone scrubbing solution was prepared by adding to each scrubber 35 ml. of a saturated brine solution, 20 ml. of distilled water, and 10 ml. of methone reagent. This reagent contained 5 grams of methone (dimethyldihydroresorcinol; 5,5-dimethyl-1,3-cyclohexanedione) in 100 ml. of 95% ethyl alcohol. Approximately 75 ml. of distilled water were used in each of the water scrubbers.

Tests on the above recovery system showed that of the products encountered in this investigation the acids, glyoxal, and formaldehyde could be quantitatively removed from the gas stream by the primary condenser and three water scrubbers and that other aldehydes and ketones which were only partially removed by these units could be completely removed by the hydrazine scrubbers. Since precipitation with this 2,4-dinitrophenylhydrazine scrubbing solution may be assumed quantitative (9), the amount of precipitate collected is a direct measure of the total amount of aldehydes and ketones removed in these scrubbers. Obviously, this method does not differentiate individual aldehydes and ketones. It has been found that acetaldehyde in the presence of ketones can be selectively and quantitatively removed from a gas stream by methone scrubbers such as those described above. With this scrubbing solution the rate of precipitation of the acetaldehyde derivative is slow but absorption of the acetaldehyde in the solution is rapid and removal is complete. Precipitation with the methone reagent is quantitative for acetaldehyde (20, 24); thus, the amount of precipitate collected is a direct measure of the acetaldehyde removed. Thus, if acetaldehyde and a single ketone are the only products present at any stage of the recovery process, the amounts of each may be determined by using both methone and hydrazine methods of recovery.

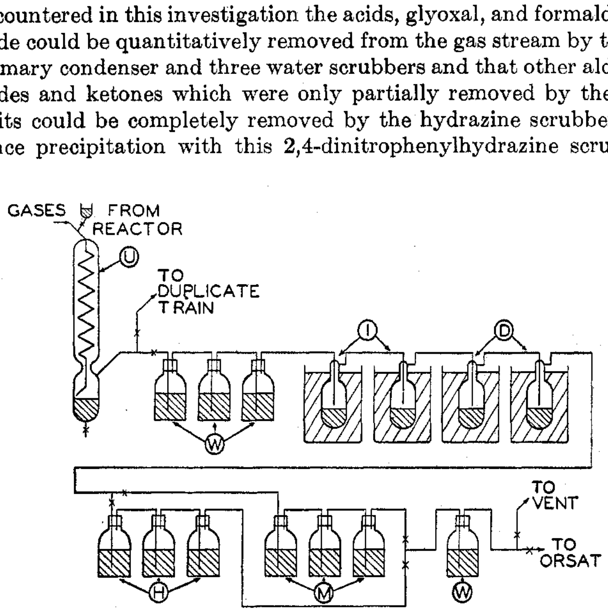


Figure 3. General Recovery Train

U. Primary water-cooled condenser
W. Water scrubbers
I. Ice traps
D. Dry-ice traps
H. 2,4-dinitrophenylhydrazine scrubbers
M. Methone scrubbers

For qualitative work all of the units shown in Figure 3 were included in the recovery system to take advantage of the greater separation of products resulting from a larger number of units. For the quantitative runs with a vanadium pentoxide catalyst different recovery systems were used for different hydrocarbons but the primary condenser and three water scrubbers were common to all of them. All of the runs with butadiene with the exception of run 91 were made with only these units. Two hydrazine scrubbers were included after the water scrubbers for run 91. This recovery system of primary condenser, three water scrubbers, and two hydrazine scrubbers was used for most of the runs with the other four-carbon hydrocarbons. Dry-ice traps were used to reduce the load on the hydrazine scrubbers for some of the high conversion runs with isobutylene and 2-butene. Methone scrubbers as well as hydrazine scrubbers were employed in the runs with 1-butene, the former being used for a portion of a run and the latter for the remainder of the run.

QUALITATIVE ANALYSIS AND IDENTIFICATION OF PRODUCTS. For the runs with the four-carbon hydrocarbons over silver or silver oxide catalysts, where only traces or small amounts of products were found, the condensates and water scrubber solutions were tested for aldehydes with Schiff's reagent and for acids with litmus paper and by titration. Specific tests were made for formaldehyde, formic acid, and acetone. The reagents used for these tests were chromotropic acid (4) and modified Schiff's reagent (3) for formaldehyde, mercuric chloride for formic acid, and salicylaldehyde (19) for acetone. For the runs with isobutylene the condensates and water scrubber solutions were tested for isobutylene glycol or oxide. In this procedure the solution was acidified with sulfuric acid to convert any oxide to glycol and then distilled to remove any acetone that may have been present originally. After acetone removal the periodate procedure (12) was used to oxidize any isobutylene glycol present to acetone and formaldehyde. A portion of this solution was distilled and the distillate tested for acetone using the salicylaldehyde procedure. Duplicate samples to which had been added small amounts of the materials being tested were run for comparison in the above tests.

Application of the above procedures indicated that only traces of aldehydes and acids were present in the products of oxidation of the four-carbon hydrocarbons when silver or silver oxide catalysts were used. The presence of formic acid and formaldehyde in trace amounts was indicated. Acetone, in more than trace amounts, was found in the oxidation of isobutylene. This compound was positively identified by means of the melting point of its 2,4-dinitrophenylhydrazone. No isobutylene oxide or glycol was indicated in any of the runs with isobutylene.

Standard procedures were used to isolate and identify the products encountered in the oxidation of the four-carbon hydrocarbons over a vanadium pentoxide catalyst.

Acetic acid and maleic acid were isolated in pure form. Acetic acid was identified by its normal boiling point and the melting point of its anilide. Maleic acid was identified by its melting point, and, after conversion, by the melting point of its isomer, fumaric acid. The other compounds found in this investigation were not isolated in pure form. In general these compounds were separated from their aqueous solutions as derivatives. The melting points of these derivatives served to identify the parent compounds. The standard mixed melting point procedure was used. The compounds identified and the derivatives employed are listed below:

Compound	Derivatives
Formaldehyde	Methone
Acetaldehyde	Methone, methone anhydride, 2,4-DNPH
α-Methylacrolein	2,4-DNPH
Glyoxal	2,4-DNPH
Methyl vinyl ketone	2,4-DNPH

In addition to the above, many confirmatory tests and procedures were employed. As a result of the above procedures products of oxidation of the four-carbon hydrocarbons were found to be as follows:

Hydrocarbon	Oxidation Products
Butadiene	Maleic acid, formaldehyde, and glyoxal
Isobutylene	Acetic acid, α-methylacrolein, and formaldehyde
1- and 2-butene	Maleic acid, acetic acid, acetaldehyde, formaldehyde, methyl vinyl ketone, and glyoxal
n-Butane	Maleic acid, acetic acid, formaldehyde, acetaldehyde (trace), and glyoxal

By similar procedures it was found that the intermediate oxidation products of acetaldehyde over a vanadium pentoxide catalyst were formaldehyde, acetic and formic (trace) acid, and of formaldehyde, formic acid.

QUANTITATIVE PROCEDURES. **Oxidation of Ethylene over a Silver Oxide Catalyst.** The analytical procedures for this phase of the investigation were the same as those used by McBee, Hass, and Wiseman (11) in their study of the oxidation of ethylene.

Oxidation of Four-Carbon Hydrocarbons over a Vanadium Pentoxide Catalyst. As explained above, a part of the over-all quantitative analysis was carried out directly in the recovery system during the run. Thus, acetaldehyde present in the gas stream beyond the water scrubbers or dry-ice traps, if the latter were used, was quantitatively recovered in the form of the methone derivative. In a similar manner volatile aldehydes and

Table I. Tabulated Results for the Oxidation of Ethylene

Catalyst III (60 cu. cm.)

Run	26A	26B	27A	27B	28	29A	29B
Air flow rate[a]	2.92	2.81	3.38	3.33	3.11	3.24	3.16
Ethylene flow rate[a]	0.202	0.107	0.181	0.190	0.207	0.156	0.222
Total flow rate[a]	3.12	2.92	3.56	3.52	3.32	3.40	3.38
Air-ethylene ratio	14.46	26.3	18.6	17.52	15.02	20.8	14.23
Contact time, seconds	1.27	1.34	1.11	1.13	1.12	1.15	1.13
Bath temperature, ° F.	532	548	529	527	589	571	569
Bed temperature, ° F.	547	553	532	528	598	579	573
Conversions, %							
Ethylene oxide	32.0	35.7	37.9	29.2	42.2	49.5	34.4
Carbon dioxide	17.4	19.7	20.3	11.5	24.7	30.7	33.9
Unreacted ethylene	49.4	44.7	40.6	54.7	36.3	18.1	32.1
Total	98.8	100.1	98.8	95.4	103.2	98.3	100.4
Yields, %							
Ethylene oxide	63.2	64.5	63.9	64.5	66.3	60.5	50.7
Carbon dioxide	34.2	35.6	33.9	25.4	38.8	37.5	50.0
Total	97.4	100.1	97.8	89.9	105.1	98.0	100.7

[a] Cubic feet per hour at standard conditions.

ketones were quantitatively recovered as 2,4-dinitrophenylhydrazones in the hydrazine scrubbers. Thus precipitation in the methone and hydrazine scrubbers results in the quantitative separation of intermediate oxidation products collected after the water scrubbers or dry-ice traps. Analysis for terminal oxidation products such as carbon dioxide and carbon monoxide in the exit gas stream was carried out by conventional gas analytical methods. The quantitative determination of the intermediate oxidation products removed prior to the hydrazine or methone scrubbers is discussed in detail below.

At the completion of a run the primary condensate, water scrubber solutions, and dry-ice condensates were mixed and made up to a definite volume with distilled water. Depending upon the results of the qualitative analysis, some or all of the following quantitative procedures were utilized in the analysis of this solution.

1. Titration with dilute alkali.
2. Precipitation of maleic acid as barium maleate monohydrate (*14*).
3. Precipitation with aqueous 2,4-dinitrophenylhydrazine. The word aqueous is used here to differentiate the alcoholic procedure described below. Actually, the precipitating agent was a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid.
4. Precipitation with alcoholic 2,4-dinitrophenylhydrazine. The precipitating agent was prepared by adding concentrated hydrochloric acid to a saturated solution of 2,4-dinitrophenylhydrazine in 95% ethyl alcohol. One ml. of concentrated hydrochloric acid was added for every 10 ml. of alcohol. The ratio of reagent to aqueous solution used was 2 to 1.
5. Precipitation with methone (*24*).
6. Colorimetric determination of formaldehyde with chromotropic acid reagent. The procedure used for this determination was essentially the same as that given by Boyd and Logan (*1*). The unknown solutions were matched against a standard in a comparison colorimeter.

Correct interpretation of the results of the above procedures depends upon information arrived at by experiments, the results of which are listed below.

Acetic acid does not interfere with the barium maleate procedure.

Procedure 4 given above is specific for glyoxal in the presence of the other aldehydes and ketones encountered in this investigation.

Glyoxal, in the low concentrations found in this investigation and under the conditions of precipitation used, does not precipitate out with the methone reagent.

None of the compounds found in this investigation interfered with the colorimetric determination of formaldehyde with chromotropic acid.

Procedure 3 removes quantitatively all aldehydes and ketones found in this investigation.

The methone procedure is not quantitative for α-methylacrolein.

Butadiene. In all runs except 91, procedure 5 was used for formaldehyde and procedure 1 for maleic acid. An analysis for glyoxal was made only in run 91. All the procedures listed above were utilized in run 91. Since the qualitative analysis showed that only maleic acid, formaldehyde, and glyoxal were present in appreciable amounts, procedures 1 and 2 should give the same results for maleic acid and procedures 5, 6, and a combination of procedures 3 and 4, likewise, should give the same results for formaldehyde. That such was the case is borne out by the actual results, expressed as per cent conversion of butadiene to the product indicated, which were as follows:

	Maleic Acid	
Procedure	1	2
Conversion, %	31.0	31.0

	Formaldehyde		
Procedure	5	6	3 and 4
Conversion, %	1.86	1.82	1.84

Isobutylene. Procedure 1 was used for acetic acid and 6 for formaldehyde. The amount of α-methylacrolein removed ahead of the hydrazine scrubbers was determined from the results of procedures 3 and 6. The precipitate in the hydrazine scrubbers was assumed to be the derivative of α-methylacrolein. This assumption was justified in view of results obtained in melting point determinations carried out with the precipitate.

2-Butene. Procedures 2, 4, and 6 were used for maleic acid, glyoxal, and formaldehyde, respectively. The amount of acetic acid present was determined from the results of procedures 1 and 2. The combined amount of acetaldehyde and methyl vinyl ketone removed ahead of the hydrazine scrubbers was determined from the results of procedures 3, 6, and 4. The combined amount of these compounds removed in the hydrazine scrubbers was determined from the weight of the precipitate in these scrubbers. For material balance purposes the results were expressed as the equivalent amount of acetaldehyde. Qualitative tests indicated that acetaldehyde was present in greater amount.

1-Butene. The amounts of maleic acid, acetic acid, formaldehyde, and glyoxal were determined in the manner described above for 2-butene. The amount of acetaldehyde removed ahead of the hydrazine or methone scrubbers was determined from the results of procedures 6 and 5. The weight of the precipitate in the methone scrubbers was a direct measure of the remaining amount of acetaldehyde. The amount of methyl vinyl ketone recovered ahead of the hydrazine scrubbers was determined from the results of procedures 3, 4, 5, and 6. The amount of acetaldehyde derivative in the precipitate in the hydrazine scrubbers was calculated from the results obtained with the methone scrubbers and the amount of the methyl vinyl ketone derivative determined by difference.

***n*-Butane.** All the procedures listed above were utilized. Procedure 2 gave results for maleic acid that were obviously too high. Total acid was given by procedure 1. The individual amounts of acetic and maleic acids were estimated from the distribution coefficient between water and ether. The results of procedures 5 and 6 indicated that the amount of acetaldehyde present was negligible. The results of procedures 3, 4, 5, and 6 indicated that no ketones were present in appreciable amounts and that the only aldehydes present were formaldehyde and glyoxal. The amount of precipitate collected in the hydrazine scrubbers was negligible.

DISCUSSION OF RESULTS

OXIDATION OF ETHYLENE OVER A SILVER OXIDE CATALYST. The runs with ethylene were made to check the performance of the experimental equipment and to determine whether or not the particular catalyst used was suitable for the oxidation of ethylene to ethylene oxide. One of the objects of this investigation was to determine the effectiveness of such a catalyst when used with the four-carbon olefins. Typical results are given in Table I. The yields and conversions given in this table are comparable to those reported elsewhere in the literature (*11, 17*). Contact times reported in this investigation are based on inlet gas composition, bath temperature, pressure on downstream side of orifice, and empty bed volume. The bed temperatures reported are approximately the maximum temperatures in the bed. The conversion of hydrocarbon to a particular product is defined as that fraction of the total amount of hydrocarbon entering the system, which by chemical reaction on an equivalent carbon basis, is converted to this product. The yield of any product is the fraction of the total amount of hydrocarbon undergoing reaction, which on an equivalent carbon basis is converted to this product. By using an equivalent carbon balance the sum of the yields and the sum of the conversions plus unreacted hydrocarbon should, theoretically, both be equal to unity or, if a percentage basis is used, to 100. The above definitions apply to all the experimental results reported in this investigation.

OXIDATION OF THE FOUR-CARBON HYDROCARBONS OVER SILVER AND SILVER OXIDE CATALYSTS. The range of variables covered and the relative amount of work done on the individual hydrocarbons in this phase of the work are summarized in Table II.

TABLE II. OXIDATION OF FOUR-CARBON HYDROCARBONS OVER SILVER AND SILVER OXIDE CATALYSTS

Ranges of variables covered

Hydrocarbons	Isobutylene	2-Butene	1-Butene	Butadiene
Number of runs	33	8	1	1
Air-hydrocarbon ratio	0.5–67	28–62	39	84
Flow rate[a]	1.5–6.5	3.4	3.6	3.8
Contact time, seconds	0.1–1.8	0.1–1.4	1.3	1.2
Bath temperature, ° F.	300–526	315–503	369–410	327–488
Bed temperature, ° F.	300–1290	315–789	367–788	325–774
Catalyst	I, II, III, IV	III, IV	IV	IV

[a] Cubic feet per hour at standard conditions.

The silver and silver oxide catalysts were quite effective in promoting the oxidation of the four-carbon hydrocarbons to carbon dioxide and water but were not suitable for the production of intermediate oxidation products. Traces of aldehydes and acids were found in most runs. The only compound found in more than trace amounts was acetone in the oxidation of isobutylene. The best conditions found for the formation of this compound were: air-hydrocarbon ratio, 8; flow rate, 3.3 cubic feet per hour at standard conditions; contact time, 1.7 seconds; and bed temperature, 400° F. Catalyst I seemed to be the best catalyst. At 400° F. only a very small fraction of the isobutylene was oxidized and the conversion to acetone was consequently very low. At higher temperatures where considerable reaction took place only traces of acetone were found. In this phase of the work good control of the bed temperature was possible only for air-hydrocarbon ratios in excess of 30. Diluting the catalyst with inert carrier and also copper shot and diluting the reactant mixture with nitrogen did not lead to the formation of intermediate products. Silver and silver oxide catalysts, although suitable for the oxidation of ethylene to ethylene oxide, do not seem to be similarly effective for the oxidation of the four-carbon olefins.

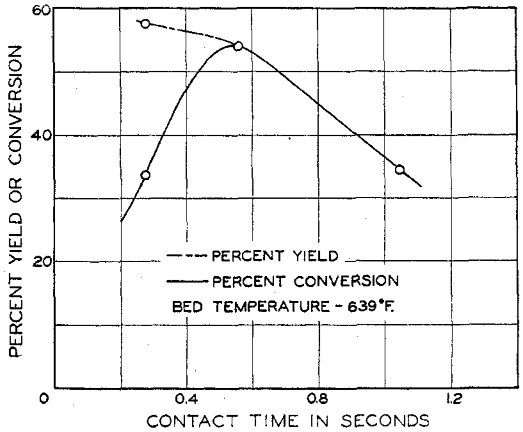


Figure 4. Effect of Contact Time on Conversion and Yield of Maleic Acid from Butadiene

Results from runs 48, 53, and 54A

OXIDATION OF FOUR-CARBON HYDROCARBONS OVER A VANADIUM PENTOXIDE CATALYST. When vanadium pentoxide, supported on Alfrax, was employed as a catalyst for the oxidation of the four-carbon hydrocarbons, appreciable amounts of intermediate products were found. The effects of the experimental variables—contact time, bed temperature, and air-hydrocarbon ratio—on the conversion and yields of products are shown graphically in Figures 4 through 9. In preparing these figures an attempt was made to include the results of only those runs in which good material balances were obtained. Nevertheless, in some cases, due to lack of sufficient data, runs with only fair material balances were utilized. No attempt was made to adjust these results to give 100% balances as it was felt that there was insufficient information as to the actual source of error. The following abbreviations are used in Figures 4 through 9: CO, carbon monoxide; CO_2, carbon dioxide; U.H.C., unreacted hydrocarbon; M.A., maleic acid; A.A., acetic acid; CH_2O, formaldehyde; α-M, α-methylacrolein; ALD., acetaldehyde (for the results with 2-butene this also includes methyl vinyl ketone calculated as acetaldehyde); and M.V.K., methyl vinyl ketone.

OXIDATION OF BUTADIENE. The results for the oxidation of butadiene over a vanadium pentoxide catalyst are given in Table III and Figures 4 and 5.

A good correlation results if percentage yield is plotted *vs.* catalyst bed temperature at constant contact time but with variable air-hydrocarbon ratio and bath temperature. This correlation is shown in Figure 5. The results of all the quantitative runs at approximately 1 second contact time are included. To show the effect of contact time, the results for maleic acid at a contact time of about $^1/_2$ second are also included. Figure 5 shows that a decrease in bed temperature at constant contact time causes a

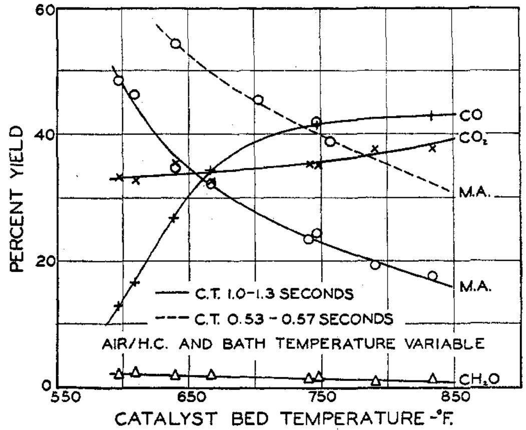


Figure 5. Effect of Catalyst Bed Temperature on Yields of Various Products from Butadiene

Results from all runs with butadiene except 54A and B

Table III. Tabulated Results for Butadiene Runs

Catalyst V

Run	42	43	46	47A	47B	48	49	50	51A[a]	51B	52	53	54A[a]	54B	91
Amount of catalyst, cc.	60	60	60	60	60	60	60	60	30	30	30	30	15	15	
Air flow rate[b]'	2.78	2.85	2.85	3.36	3.46	3.43	3.44	3.32	3.36	3.36	3.09	3.32	3.33	3.27	2.90
Hydrocarbon flow rate[b]	0.0559	0.0595	0.0750	0.0917	0.0969	0.0557	0.0397	0.0290	0.0589	0.0588	0.0630	0.0263	0.0337	0.0259	0.0808
Total flow rate[b]	2.84	2.91	2.93	3.45	3.56	3.49	3.48	3.35	3.42	3.42	3.15	3.35	3.36	3.30	2.98
Air-hydrocarbon ratio	49.7	47.9	38.0	36.6	35.7	61.5	86.6	114.6	57.1	57.1	49.0	126.3	98.8	126.3	35.9
Contact time, seconds	1.32	1.28	1.27	1.05	0.97	1.04	1.07	1.12	0.54	0.53	0.57	0.56	0.28	0.27	0.96
Bath temperature, ° F.	594	585	585	623	664	602	589	581	590	610	612	596	598	630	664
Bed temperature, ° F.	790	740	666	747	833	639	609	597	702	746	757	639	639	692	792
Conversions, %															
Carbon dioxide	37.9	35.5	32.7	35.1	37.9	35.4	32.9	33.4	20.1	26.5	25.6	25.9	11.6	23.2	24.1
Carbon monoxide	[c]	[c]	34.5	41.7	43.0	27.0	16.8	13.0	6.4	13.65	34.5	30.0	10.4	23.2	39.2
Maleic acid	19.33	23.6	32.3	24.6	17.8	34.9	46.2	48.7	37.9	42.0	39.0	54.2	33.7	46.2	31.0
Formaldehyde	0.68	1.06	1.99	1.50	1.03	1.90	2.33	2.06	2.56	2.94	2.80	3.06	2.40	3.50	1.84
Unreacted hydrocarbon	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	16.40	0.00	0.00	0.00	41.6	0.00	0.00
Total			101.5	102.9	99.7	99.2	98.2	97.2	83.4[d]	85.1[d]	101.9	113.2	99.7	96.1	98.7[e]

[a] Yields, run 51A: CO_2, 24.1; CO, 7.6; M.A., 45.4; CH_2O, 3.07; total, 80.2. Run 54A: CO_2, 19.8; CO, 17.8; M.A., 57.7; CH_2O, 4.14; total, 99.4.

[b] Cubic feet per hour at standard conditions.

[c] No analysis for carbon monoxide made.

[d] CO analyses believed to be in error.

[e] Conversions to glyoxal 0.24%, and to other unidentified products approximately 2.4%.

pronounced increase in the yield of maleic acid, a slight increase for formaldehyde, a pronounced decrease for carbon monoxide, and a slight decrease for carbon dioxide. Also indicated is an increase in the yield of maleic acid with a decrease in contact time. This effect is shown in more detail in Figure 4. Thus, it is seen that the yield of maleic acid decreases with an increase in contact time, and the conversion of hydrocarbon to maleic acid initially increases, passes through a maximum, and then decreases. The experimental point corresponding to approximately the maximum conversion may be high in view of the material balance for this run (113%), but this would not seriously affect the trend described above.

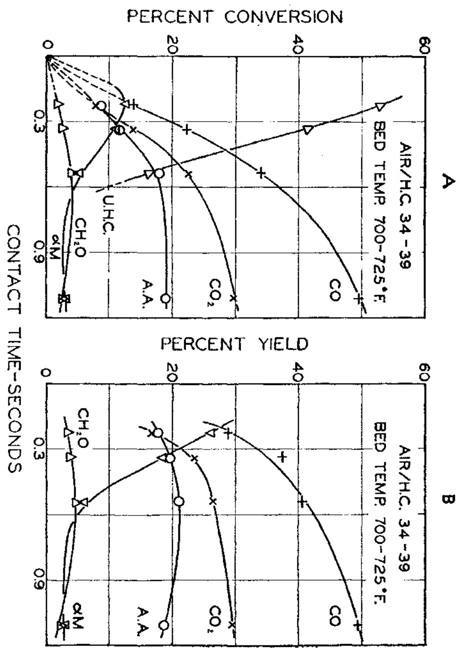


Figure 6. Effect of Contact Time on Conversions and Yields of Various Products from Isobutylene

Run 91 was made after approximately 8 months of operation to determine the effect of catalyst age on conversion and yields. This effect is shown by the comparison with runs 47A and 47B.

Run	91	47B	47A
Air-hydrocarbon ratio	35.9	35.7	36.6
Contact time, seconds	0.96	0.97	1.0
Bath temp., ° F.	664	664	623
Bed temp., ° F.	792	833	747
Conversions			
Maleic acid	31.0	17.8	24.6
Formaldehyde	1.8	1.0	1.5
Glyoxal	0.2		
Carbon monoxide	39.2	43.0	41.7
Carbon dioxide	24.1	37.9	35.1
Others	2.4		
Total	98.7	99.7	102.9

Better conversions of hydrocarbon to maleic acid were obtained with the old catalyst. If there were no effect of catalyst age, it would be expected that the conversion to maleic acid would be less for run 47B than for run 91 in view of the higher bed temperature but not to the extent indicated. Applying the same reasoning, the conversion to maleic acid in run 47A should be greater than that in run 91 in view of the lower bed temperature. Actually it is appreciably less.

This improvement in maleic acid yield or conversion with catalyst age has recently been reported by Nielsen (*15*) in his study of the vapor-phase oxidation of furfural.

The highest conversion of butadiene to maleic acid was somewhat greater than 50% under conditions of low bed temperature and high air-hydrocarbon ratio. The highest yield found was about 58% under conditions of high air-hydrocarbon ratio, low bed temperature, and short contact time. The conversion under these conditions, however, was only 34%.

Oxidations of Other Hydrocarbons. Some of the results obtained with the other hydrocarbons are shown in Figures 6 through 9. The effect on conversions and yields of increasing the air-hydrocarbon ratio, other conditions being constant, is shown in Figures 8*A* and 8*B*. Increasing this ratio causes an ap-

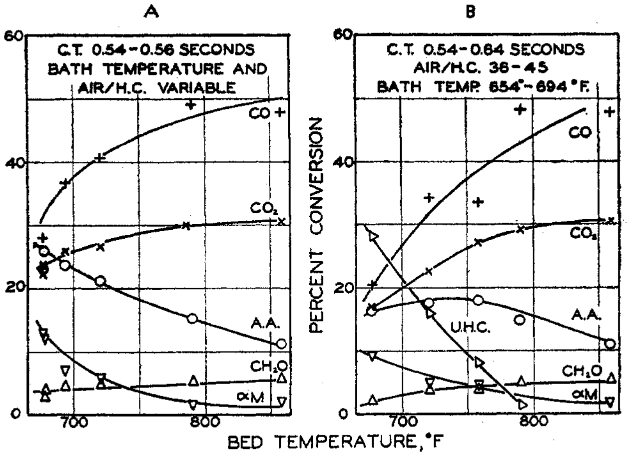


Figure 7. Effect of Bed Temperature on Conversions and Yields of Various Products from Isobutylene

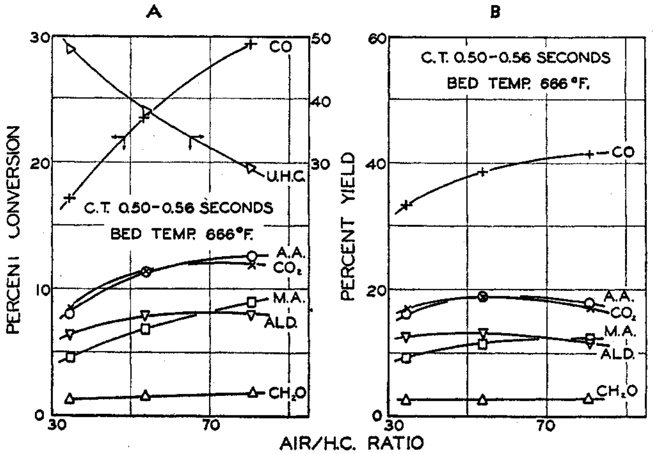


Figure 8. Effect of Air-Hydrocarbon Ratio on Conversions and Yields of Products from 2-Butene

preciable increase in conversion of hydrocarbon to intermediate products. The effect on yields is much less. Since the material balance for the yields corresponding to the lowest air-hydrocarbon ratio was about 10% low, the small initial upward trends are probably not significant. This small effect on yields explains the good correlation obtained in Figure 5 for butadiene in which the air-hydrocarbon ratio was variable. A similar correlation is shown for isobutylene in Figure 7*A*. Since the yields are little affected by an increase in the air-hydrocarbon ratio, the observed increases in conversions are due to an increase in the fraction of hydrocarbons undergoing reaction.

The effect of increasing the bed temperature, other conditions being the same, is shown for isobutylene in Figures 7*A* and 7*B*. In general, an increase in bed temperature causes a decrease in yield of intermediate products, an increase in yield of terminal products, carbon monoxide and carbon dioxide, and an increase in the fraction of hydrocarbon undergoing reaction. The effect on conversion to any particular intermediate will depend upon the relative magnitudes of the effects on yield and fraction of hydrocarbon reacting. Thus, the conversion of isobutylene to acetic acid (Figure 7*B*) actually increases with temperature initially and then falls off again at high temperatures, whereas the yield for acetic acid (Figure 7*A*) decreases continuously with increasing temperature. It was also observed that the temperature effect was more pronounced at short contact times.

The variations of conversions and yields with contact time are shown in Figures 6*A*, 6*B*, 9*A*, and 9*B*, where it is seen that the conversion of hydrocarbon to intermediate products initially increases, reaches a maximum, and then decreases as the contact time increases. The final decrease is not evident for some of the compounds in the range of contact times studied. In general, the maximum conversions for acids occur at greater contact times than those for aldehydes. In many cases the yield of intermediate products increased with a decrease in contact time.

The magnitudes of the various yields and conversions are evident from Figures 6*A* through 9*B*. The results obtained for 2-butene were quite similar to those obtained for 1-butene. However, less acetic acid and acetaldehyde and more methyl vinyl ketone and maleic acid were obtained with 1-butene, the increase in maleic acid being slight. The amount of glyoxal present was always quite small and for this reason results for this compound have been omitted from the various figures. In most runs both conversions and yields for glyoxal were less than 1%.

n-Butane proved to be quite resistant to oxidation over a vanadium pentoxide catalyst. No reaction occurred below a temperature of 690° F. and there was only a gradual increase in the extent of the reaction in the temperature range 690° to 820° F. At a contact time of about 1 second, bed temperature of 822° F., and air-hydrocarbon ratio of 36, only about 7% of the hydrocarbon reacted, of which less than 1% went to intermediate products. The following approximate yields were obtained under these conditions.

	Yield, %
Carbon dioxide	20.0
Carbon monoxide	69.9
Formaldehyde	3.5
Acids	6.4
Glyoxal	0.2
Total	100.0

The acids present were mainly acetic and maleic, the latter being present in greater amount.

Oxidation of Other Compounds. The oxidation of carbon monoxide, hydrogen, formaldehyde, and acetaldehyde have been investigated. It was hoped that such an investigation would yield results which would be helpful in interpreting the results of the oxidation of the four-carbon hydrocarbons and which might indicate a mechanism of oxidation over the catalyst used. Catalyst V was used for this phase of the work. The following average conditions held during these runs.

	Carbon Monoxide	Hydrogen	Acetaldehyde	Formaldehyde
Composition, % by volume	3.0	4.0	1.0	1.7
Flow rate, cu. ft. per hr. at standard conditions	3.0	3.5	3.0	2.7
Contact time, seconds	1.0	0.9	1.0	1.2
Bed temperature, ° F.	608–655	563–693	610–627	580

No reaction occurred with either carbon monoxide or hydrogen, Acetaldehyde was easily oxidized under the above conditions. Conversion to 80.0% carbon monoxide, 7.0% carbon dioxide.

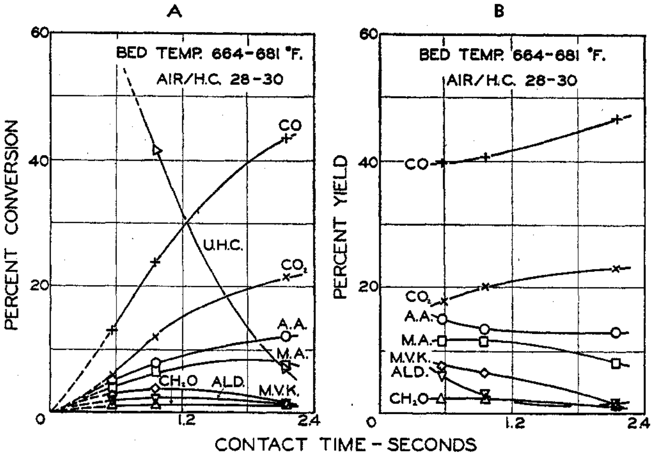


Figure 9. Effect of Contact Time on Conversions and Yields of Products from 1-Butene

5.0% formaldehyde, and 8.0% acetic acid (total 100.0%) was obtained.

A small amount of formic acid was also found. This has been included with the acetic acid.

Formaldehyde was also readily oxidized under the above conditions. Only carbon monoxide and a small amount of formic acid were found as oxidation products. It is estimated that at least 95% of the formaldehyde was oxidized to carbon monoxide. No carbon dioxide was detected. Thus, it is seen that the oxidation of these aldehydes under the above conditions leads predominantly to carbon monoxide as a product.

MECHANISM

The products found in the vapor-phase oxidation of the four-carbon hydrocarbons over a vanadium pentoxide catalyst can for the most part be explained by a scheme of atomic dehydrogenation and peroxidation similar to that suggested by Waters (*23*) and by peroxide decomposition. The first step in this scheme would be the removal of a hydrogen atom from the hydrocarbon forming a free radical which then could react with a molecule of oxygen to form a peroxide radical. This last product could then become a peroxide by gaining a hydrogen atom. In the scheme proposed by Waters the peroxide radical abstracts a hydrogen atom from another hydrocarbon molecule and the reaction proceeds in a chain fashion. In the present system of heterogeneous catalysis, the vanadium pentoxide catalyst evidently plays an important role, the nature of which is not disclosed by the results of this investigation. To explain the results which have been reported it is suggested that the catalyst be considered as a hydrogen atom abstractor and donator. This role of the catalyst is then represented by the reaction

$$RH + X \longrightarrow HX + R{-} \quad (1)$$

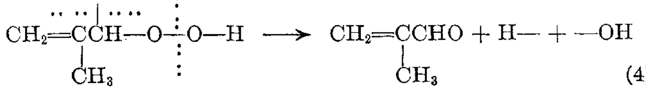
$$R{-} + O_2 \longrightarrow R{-}O{-}O{-} \quad (2)$$

$$R{-}O{-}O{-} + HX \longrightarrow ROOH + X \quad (3)$$

where X represents the catalyst.

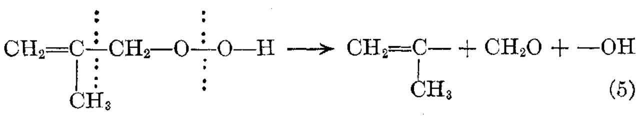
The mode of decomposition of the peroxides of saturated hydrocarbons has been discussed by Walsh (*21*) and George and Walsh (*7*). The little information available on the decomposition of peroxides of unsaturated hydrocarbons has been summarized by Farmer (*6*). Evidence indicates that decomposition of peroxides occurs by scission at the O—O bond followed by scission of an adjacent C—H bond or of the weakest adjacent C—C bond.

The presence of α-methylacrolein and methyl vinyl ketone in the products of oxidation of isobutylene and 1-butene, respectively, indicate that the initial point of oxidative attack on the mono-olefins may be at the α-methyl or methylenic carbon atom. With this initial point of attack, an attempt will now be made to explain the results obtained in the oxidation of isobutylene. The first step would involve the formation of the hydroperoxide by Equations 1, 2, and 3, the peroxide group being attached to one of the alpha carbon atoms. The second step would involve the decomposition of this peroxide. Scission of the O—O bond and adjacent C—H bond could lead to α-methylacrolein.



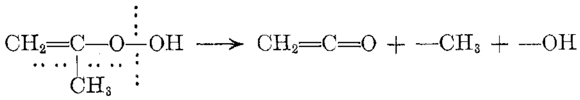
$$CH_2{=}\underset{CH_3}{C}\overset{H}{C}H{-}O{-}O{-}H \longrightarrow CH_2{=}\underset{CH_3}{C}CHO + H{-} + {-}OH \quad (4)$$

If scission at the adjacent C—C bond rather than at the C—H occurs, formaldehyde and another radical could result.



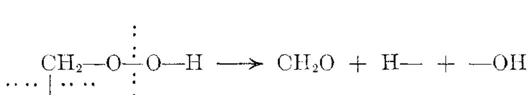
$$CH_2{=}\underset{CH_3}{C}{-}CH_2{-}O{-}O{-}H \longrightarrow CH_2{=}\underset{CH_3}{C}{-} + CH_2O + {-}OH \quad (5)$$

This new radical would then by Equations 2 and 3 be converted to a peroxide which could decompose.



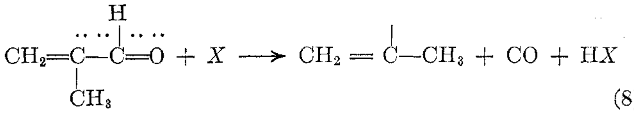
$$CH_2{=}\underset{CH_3}{C}{-}O{-}OH \longrightarrow CH_2{=}C{=}O + {-}CH_3 + {-}OH \quad (6)$$

Any ketene formed by Equation 6 would be hydrated to acetic acid in the final product. Formaldehyde could also be produced by peroxidation of the methyl radical and subsequent decomposition of the peroxide.



$$\underset{H}{CH_2}{-}O{-}O{-}H \longrightarrow CH_2O + H{-} + {-}OH \quad (7)$$

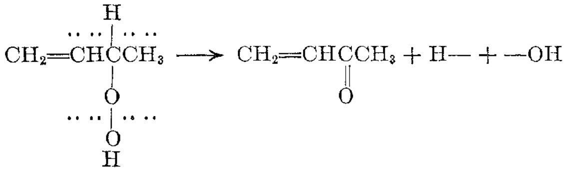
The results of the work with acetaldehyde and formaldehyde indicate that aldehyde oxidation results in the formation of large amounts of carbon monoxide. This reaction for α-methylacrolein could be represented by



$$CH_2{=}\underset{CH_3}{C}{-}\overset{H}{C}{=}O + X \longrightarrow CH_2 = \overset{|}{C}{-}CH_3 + CO + HX \quad (8)$$

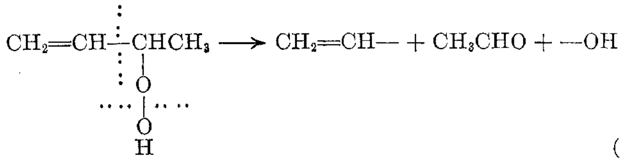
Oxidation of the radical would then proceed by reactions given above. This scheme would account for the products of oxidation of isobutylene.

In a reaction similar to Equation 4 methyl vinyl ketone could be formed from the peroxide resulting from the oxidation of 1-butene.



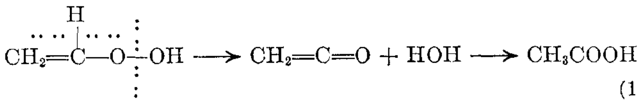
$$CH_2{=}CH\overset{H}{\underset{\substack{O\\|\\O\\H}}{C}}CH_3 \longrightarrow CH_2{=}CH\underset{\substack{\|\\O}}{C}CH_3 + H{-} + {-}OH \quad (9)$$

Another mode of decomposition would be



$$CH_2{=}CH{-}\underset{\substack{O\\|\\O\\H}}{C}HCH_3 \longrightarrow CH_2{=}CH{-} + CH_3CHO + {-}OH \quad (10)$$

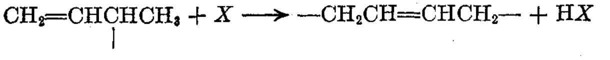
This would account for the acetaldehyde found. The results given previously show that acetaldehyde is not in itself the major source of acetic acid. The results for isobutylene show that acetaldehyde is not a necessary intermediate for this compound. Most of the acetic acid found could come from the oxidation of the radical resulting from Equation 10. After forming a peroxide the reaction



$$CH_2{=}\overset{H}{C}{-}O{-}OH \longrightarrow CH_2{=}C{=}O + HOH \longrightarrow CH_3COOH \quad (11)$$

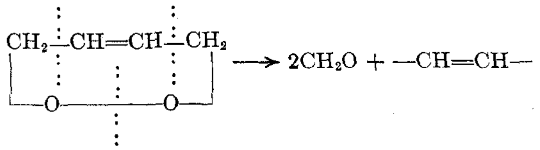
could occur.

Further oxidation of acetaldehyde would yield carbon monoxide and formaldehyde by Equations 8 and 7. In addition apparently a small amount of acetic acid is formed, probably through the intermediate formation of peracetic acid. Thus far, methyl vinyl ketone, acetaldehyde, acetic acid, and formaldehyde have been accounted for. The presence of maleic acid and glyoxal is explained by a different series of reactions. Instead of Equation 2 immediately following Equation 1 another atomic dehydrogenation similar to that occurring in Equation 1 could occur. For 1-butene the following di-radical could be formed.



$$CH_2{=}CH\underset{|}{C}HCH_3 + X \longrightarrow {-}CH_2CH{=}CHCH_2{-} + HX \tag{12}$$

According to Farmer (*6*) such a compound could form a cyclic peroxide which in turn could decompose



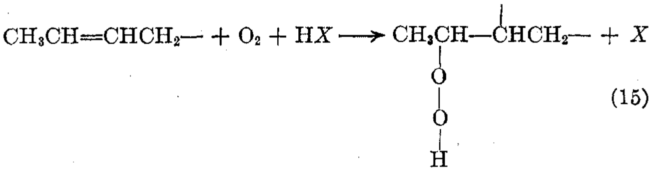
(13)

The resulting di-radical may be the source of glyoxal.

$$-CH{=}CH- \; + \; O_2 \longrightarrow CHOCHO \tag{14}$$

No attempt will be made to indicate the exact mechanism for the formation of maleic acid or anhydride, but it is apparent that oxidation at the ends of the conjugated system without scission of the carbon chain could lead to these compounds. Neither maleic acid nor glyoxal was found in the oxidation of isobutylene, which is explained by the inability of this hydrocarbon to form a conjugated system by hydrogen removal. The results for butadiene are also explained by the reactions given above. Since fewer steps are required to produce maleic acid from butadiene than from 1- or 2-butene, the yields and conversions from the former should be greater. This was found to be true.

If the scheme given above is applied to 2-butene, one would expect crotonaldehyde as a product. This compound was not found in this investigation. One way by which the actual results can be explained is that after the initial removal of a hydrogen atom peroxidation occurs not at the alpha carbon atom but at the double bond.

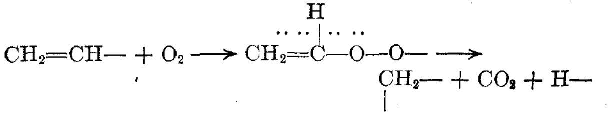


$$CH_3CH{=}CHCH_2{-} + O_2 + HX \longrightarrow CH_3\underset{\substack{|\\ O\\ |\\ O\\ |\\ H}}{CH}{-}\overset{|}{C}HCH_2{-} + X \tag{15}$$

Obviously, this peroxide could stabilize by a double bond formation in the 1 position and reactions identical to those described for 1-butene would result. However, more acetaldehyde and acetic acid and less methyl vinyl ketone were found with 2-butene. This would indicate that the above peroxide more readily decomposes by scission of the carbon chain at the 2 position possibly before a shifting of the double bond to the 1 position occurs.

The absence of an alpha carbon atom explains the low reactivity of *n*-butane. The products found in the oxidation of this hydrocarbon can be accounted for by reactions similar to those given above. In order to obtain maleic acid from *n*-butane a series of dehydrogenations similar to those described above must occur.

As yet no mention has been made of a reaction resulting in the formation of carbon dioxide. The work with carbon monoxide, acetaldehyde, and formaldehyde shows that carbon monoxide itself is not oxidized to any appreciable extent over a vanadium pentoxide catalyst. The work with the four-carbon hydrocarbons shows that under similar conditions of operation the greater the degree of unsaturation in the original hydrocarbon the greater is the amount of carbon dioxide relative to carbon monoxide formed. There is some indication that the carbon dioxide formation is associated with the formation of acids. For example, the reaction



$$CH_2{=}CH{-} + O_2 \longrightarrow CH_2{=}\overset{\substack{H\\ |}}{C}{-}O{-}O{-} \longrightarrow \underset{|}{C}H_2{-} + CO_2 + H{-} \tag{16}$$

might occur. Oxidation of the above radical to give acetic acid has already been discussed. In the oxidation of 1- and 2-butene an upward trend in the yield of carbon dioxide is accompanied by a corresponding decrease in the yield of acetic acid. The above reaction is also in agreement with the observed effect of unsaturation mentioned above.

The formation of water in the oxidation of these hydrocarbons probably comes from the combination of the hydroxyl radical and hydrogen atoms. The work with hydrogen shows that any molecular hydrogen formed probably would not be oxidized to water. Failure of the vanadium pentoxide to catalyze the reaction with molecular hydrogen is probably due to the greater bond strength of the H—H bond as compared with the C—H bonds of the hydrocarbons.

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Correction

A typographical error appeared in the paper "Burning Velocities. Acetylene and Dideuteroacetylene with Air" [Raymond Friedman and Edward Burke, Ind. Eng. Chem., **43,** 2772–6 (1951)]. The last column of Table I should be headed kK'/kK' instead of K/K'.

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