The Vapor Phase Oxidation of 1, 3-Pentadiene

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THE VAPOR PHASE OXIDATION OF 1,3-PENTADIENE

BY

DAVID E. SASSER
B.S., Florida Technological University, 1976

RESEARCH REPORT

Submitted in partial fulfillment of the requirements for the degree of Master of Science: Industrial Chemistry in the Graduate Studies Program of the College of Natural Sciences of Florida Technological University

Orlando, Florida
1978
ABSTRACT

The vapor phase oxidation of 1,3-pentadiene, over heterogeneous catalysts, was investigated with the objective of producing 2,4-pentadienal and 2,4-pentadienoic acid. Copper and cobalt-molybdenum catalysts, both supported and unsupported, were utilized at various reaction temperatures, residence times and feed ratios.

The manner of 1,3-pentadiene vaporization and introduction into the reactor system proved to be critical. Low temperature vaporization of the hydrocarbon and dilution with the oxidant, air, was found to be necessary to avoid polymerization of the feed.

Alumina-supported catalysts were found to be very active, leading to severe cracking of the hydrocarbon feed and subsequent carbonization of the catalysts. Silica-supported catalysts did not suffer from this problem.

At all conditions studied the oxidations were non-selective, with numerous products being observed. The desired product, 2,4-pentadienoic acid, was observed only in trace amounts over cobalt molybdate. 2,4-Pentadienal was observed over all catalysts. The highest yield of 2,4-pentadienal, 11%, occurred over cobalt molybdate.
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INTRODUCTION

Purpose - Piperylene Oxidation

Dow Chemical U.S.A. has an interest in improving the value of some of the by-products obtained during the cracking of naphtha to ethylene. The aim of this research project was to concentrate on one such by-product, 1,3-pentadiene (piperylene), and to consider an oxidation scheme to produce certain oxygen containing compounds which could be used in synthesizing derivatives with potential market value. To this end, the heterogeneous vapor phase allylic oxidation of piperylene was studied, with the emphasis placed on the production of the carboxylic acid.

\[
\begin{align*}
\text{CH}_2=\text{CH}-\text{CH}=&\text{CH}-\text{CH}_2 & [0] & \text{CH}_2=\text{CH}-\text{CH}=&\text{CH}_2\text{OH} \\
\text{CH}_2=\text{CH}-\text{CH}=&\text{CH}_2\text{CHO} \\
\text{CH}_2=\text{CH}-\text{CH}=&\text{CH}_2\text{COOH}
\end{align*}
\]

In an attempt to evaluate the types of catalysts and reaction conditions to be employed for this oxidation, a short review will be presented on the heterogeneous oxidation of propylene, C\text{\textsubscript{4}} olefins, and the C\text{\textsubscript{5}} olefins.

Oxidation of Propylene

In 1948, Hearne and Adams\textsuperscript{1} showed that propylene could be selectively oxidized to acrolein over a copper oxide catalyst. This discovery gave rise to the commercial process of catalytic oxidation of olefins to aldehydes and various other carbonyl compounds. Since
that time numerous metal oxides and mixed metal oxides have been investigated as catalysts for the oxidation of olefins.

Over copper oxide catalysts, propylene is selectively oxidized to acrolein only when a relatively high olefin to oxygen ratio is maintained. Studies performed by Isaev and co-workers, Popova and Vermel, Ghorokhovatskii et al., and others indicate that the selectivity over a copper oxide catalyst is dependent upon the chemical composition of the catalyst which is in turn heavily dependent upon the reaction medium. The most active catalyst surface for acrolein formation is one which consists of a copper rich cuprous oxide. In the temperature range of 300-400°C, cuprous oxide is readily oxidized or reduced. A catalyst containing principally copper or cupric oxide as the solid phase gives poorer results (cupric oxide favors complete oxidation of propylene). With the need to maintain the cuprous oxide state, the best results are obtained with a propylene to oxygen volume ratio in excess of four. Under these conditions, typical conversion per pass of propylene is about 10-20%, and selectivity to acrolein is often on the order of 60-85%. In addition to the formation of acrolein, a number of by-products are also produced, such as, carbon oxides (large amounts), propionaldehyde, acetone, acetaldehyde, allyl alcohol, formaldehyde, and acetic acid.

In the presence of certain additives, such as halogens, halogenated compounds, and selenium compounds, a pronounced enhancement in the selectivity of the oxidation may occur. For example,
Holbrook and Wise\(^5\) have reported on the promoter action of methyl bromide in the oxidation of propylene over a copper catalyst. At an oxygen partial pressure of 100 torr, the ratio of acrolein to carbon oxides \((\text{[acrolein]}/\text{[CO} + \text{CO}_2])\) increased from 0.011 in the absence of methyl bromide to 0.39 in the presence of methyl bromide. This marked increase in the selectivity of the oxidation was attributed to the ability of the promoter, methyl bromide, to prevent the oxidation of cuprous oxide to cupric oxide and thus allows operating at a lower propylene to oxygen ratio. Similar results were observed when small amounts of selenium vapors were passed with propylene over a copper catalyst\(^6\). At less than 2\% by volume propylene in air over the selenium containing catalyst (5-10\% Se) very high selectivity to acrolein was observed at conversions as high as 80\%. At these conditions in the absence of selenium, the product is almost entirely carbon dioxide. It appears from work by Kominami and co-workers\(^7-8\), that selenium is not a promoter in this modified copper oxide catalyst; rather the active phase of the catalyst is a compound of copper and selenium, such as CuSeO\(_2\). One considerable drawback in using a selenium based catalyst is the need for recovery and recycle of the selenium due to the volatility of selenium at the conditions necessary for oxidation. This coupled with the low abundance of the element makes it doubtful whether a selenium based catalyst could ever be used on a commercial scale.

Cuprous oxide is the only useful single metal oxide catalyst for the oxidation of olefins, with the possible exception of
vanadium pentoxide. All other useful heterogeneous oxidation catalysts are of a mixed oxide composition and it appears that there is a synergistic effect that occurs with the combination of two or more oxides. This characteristic of heterogeneous oxidation catalysts can be best understood by considering the redox mechanism first proposed by Mars and Van Krevelen\(^9\). In this theory\(^10\), the catalytic action occurs in two steps - (1) reduction of the catalyst by the olefin and, (2) oxidation of the reduced catalyst by oxygen.

The olefin is adsorbed on a site \(M_1\) having the character of an electron acceptor to form a chemisorbed species, a surface \(\pi\)-complex. The olefin then undergoes oxidation at the expense of the group present at site \(M_1\) with the electrons produced being transferred toward a second site \(M_2\) which undergoes reduction and becomes an electron-donor site on which molecular oxygen can be adsorbed for the reoxidation of the catalyst. From the above scheme, it can be seen that the presence of cationic sites on the catalyst surface is a necessary condition for selective oxidation and this is provided by a mixed oxide catalyst. Thus on mixed oxides, the olefin is assumed to be adsorbed on the cations of the oxide with the highest valance and the role of the auxiliary cation is to reoxidize the principle cation and to transfer electrons to the molecular oxygen. In cuprous oxide and vanadium oxide catalysts, the two active sites are provided by the ability of copper and vanadium ions to coexist in different valance states under the conditions employed for oxidations.
In 1959, Standard Oil Company (Ohio) received a patent\textsuperscript{11} on a catalyst consisting of bismuth and molybdenum oxides, which was quite selective for the oxidation of propylene to acrolein at high conversions. This catalyst had the added advantage of operating at low propylene to oxygen ratios without the necessity of using volatile promoters. For example, Veatch and co-workers\textsuperscript{12} reported that when a feed with a low propylene to oxygen ratio of 0.5 was passed over a bismuth phosphomolybdate catalyst at 450°C, a 60% yield of acrolein was obtained at a conversion of 92%. The presence of phosphoric acid is not required but does enhance the performance of the catalyst. From the extensive work devoted to the study of bismuth molybdate catalysts, it appears that this catalyst functions most efficiently in the composition range of Bi/Mo 2/3 to 2/1. There is disagreement on the optimum composition for the catalyst—that of a Bi/Mo ratio of 1/1\textsuperscript{13},\textsuperscript{11} or 2/1\textsuperscript{15}. In addition to the formation of acrolein, several by-products are also produced in the oxidation of propylene to acrolein over bismuth molybdate catalysts, such as carbon oxides, propionaldehyde, acetaldehyde, propionic, formic, and acetic acids.

After the discovery of the bismuth molybdate catalysts, a large number of modified bismuth molybdates were investigated. These modified catalysts were derived from the basic Sohio catalyst by the addition of other components in an effort to improve the selectivity of the catalyst. Initially these modified catalysts were developed by the addition of a single additive, followed by the use of more than one additive. Common additives which have been used
are P, Fe, Ni, Co, Sm, Ta, As, B, Si, V, Sb, Ba, and Te.

In addition to the bismuth molybdate based catalysts, many other mixed metal oxide catalysts have been used in the oxidation of propylene to acrolein. One such catalyst is the tin-molybdenum system. Pluta and Blasiak\textsuperscript{16} have investigated the oxidation of propylene over such a system and have found that in the temperature range of 310-420°C, the most effective catalyst composition occurs at molybdenum-tin ratios of 85.2/17.7 and 65.5/36.5 with a conversion of only 8% with a 40-50% yield of acrolein. On the other hand, Lazukin \textit{et al.}\textsuperscript{17} reported a selectivity of 79% to acrolein over catalysts with molybdenum to tin ratios of 1:9 and 9:1.

Tin-antimony oxide catalysts have also been used in the oxidation of propylene to acrolein. This catalyst has similar properties to that of bismuth molybdates. For example, Lazukin and co-workers\textsuperscript{18} have shown that over such a catalyst with a tin to antimony ratio of 75:25, that a selectivity to acrolein and acetaldehyde of 95% was observed. Other antimony based catalysts used in the oxidation of propylene to acrolein are: antimony-uranium oxides\textsuperscript{19} and bismuth-antimony oxides\textsuperscript{20-21}.

In the oxidation of propylene to acrolein, a significant amount of acrylic acid has been produced over certain catalysts. This and the discovery during the late 1950's, that several catalysts could be used to selectively oxidize acrolein to acrylic acid encouraged many workers to search for a catalyst which would yield acrylic acid directly from propylene.
Catalysts used in the production of acrylic acid are commonly grouped into three categories. Group I catalysts are mild oxidation catalysts which are used for the production of acrolein from propylene. With these catalysts only a small amount of acrylic acid is produced in conjunction with the acrolein. Group II catalysts give simultaneous production of acrolein and acrylic acid in the oxidation of propylene. Catalysts which produce acrylic acid from the oxidation of acrolein compose group III.

The majority of catalysts in group II are derived from cobalt molybdates. Oxide compounds of W, Te, Sb, Bi, Si, Fe, Sn, and Cu have been incorporated into the catalysts in order to increase the selectivity toward acrylic acid. It has been determined that in the oxidation of propylene to acrylic acid, the atomic ratio of molybdenum to cobalt must be within 1.5-2.0 for sufficient production of acrylic acid, with the optimum occurring at a ratio of \(1.7\). For example, Isaev and Margolis\(^2^4\) reported that over a \(\text{Co}_6\text{Mo}_{12}\text{Bi}_{0.5}\text{Fe}_{0.5-1.0}x\) catalyst at 400°C and a contact time of 3.6 seconds, a mixture of 5-7 volume % of propylene, 65-65% air, and 30% steam resulted in a propylene conversion of 98-99%, at acrylic acid and acrolein yields 50-52 and 50-55% respectively.

Modified bismuth molybdates are another type of group II catalysts. Some of the various modifiers used are oxides of Fe, P, Ag, Co, Ni, Sb, W, Ti, Sn, V, B, and Te. Hirota and co-workers\(^2^5\), studied the oxidation of propylene over a catalyst containing oxides of molybdenum, bismuth, and vanadium at 400°C. With a feed
composition of 15% propylene, 4.8% oxygen, 11.5% nitrogen, and 68.7% steam, a propylene conversion of 12% was observed with selectivities of 67% for acrylic acid and 34% acrolein. Over these catalysts and also cobalt molybdates, several by-products are formed in addition to acrolein and acrylic acid. Some of these by-products are acetic acid, acetaldehyde, carbon oxides, propionic acid, formic acid, formaldehyde, and acetone.

Cobalt molybdates and bismuth molybdates have the disadvantage that acrolein is coproduced with acrylic acid. There are several group II catalysts which can produce acrylic acid with only traces of acrolein as a side product. However, acetic acid becomes a significant by-product. One of these catalyst systems contains 5-10% arsenic pentoxide, 10% niobium pentoxide (or tantalum pentoxide) and 20% molybdenum oxide supported on silica. At 400°C with a mixture of 9% propylene, 65% air, and 20% steam, conversions to acrylic acid of up to 20 mole % are obtained in a single pass, the yield of acrylic acid being about 50 mole %. The major disadvantage in this catalyst system, is the tendency of the catalyst to lose arsenic as As₂O₃ during service, but by adding As₂O₃ to the feed, stable activity could be maintained for over 1100 hours.

A few catalysts which do not fall into the above categories, that are used in the oxidation of propylene to acrylic acid are derivatives of antimony-vanadium, tungsten-vanadium and molybdenum-tellurium oxides. One such catalyst, a MoTeNiCrSi (4:2:1:1:2.5) combination is capable of oxidizing propylene at a 67% conversion
at 430°C to acrylic acid and acrolein with yields of 83% and 10% respectively.

Group III catalysts, useful for the conversion of acrolein to acrylic acid, most commonly consist of mixed oxides such as, Mo-P, Mo-Bi, Co-Mo, Mo-V, Mo-Sb, Mo-W, Mo-Cr, Mo-Tl, V-Cu, P-V, and W-P. For example, Honda et al.\textsuperscript{27} reported a 99% conversion of acrolein over a Mo-Tl-Re (1:0.1:0.1) oxide catalyst at 510°C in the presence of steam with a selectivity to acrylic acid of 85%.

For the conversion of propylene to acrylic acid, it might appear that a suitable catalyst could be formed by the mixing of a group III catalyst with one of either group I or group II. In the mixing of the catalyst components, it is likely that a new phase is formed and hence a new catalyst formed since the properties of oxide catalysts are not additive\textsuperscript{28}. In several patents, components of group I and group III have been mixed, without significantly improved selectivity.

In most of the processes where acrylic acid is produced from propylene, two catalysts are used either in the same reactor or in separate reactors. BASF has developed a two reactor system which gives good yields of acrylic acid\textsuperscript{29}. The first reactor contains a catalyst consisting of a Mo-W-Te oxide mixture supported on steatite (the loading of the catalyst is progressively increased from the reactor to its exit to enhance the activity) in which a propylene-air-steam mixture (120:1440:600 l/h) is converted to acrolein. The acrolein stream from the first reactor is fed to a second reactor
in which acrolein is converted to acrylic acid at 255°C over a Mo-W-V-Fe on steatite catalyst (also of increasing loading). This results in a propylene conversion per pass of 94 mole %, with an acrylic acid yield of 60 mole %. The use of a two catalyst system in the manufacture of acrylic acid from propylene appears to be preferred at present due to the lack of an ideal single catalyst system.\(^{50-52}\).

Oxidation of C\(_4\) Olefins

The oxidation of the four carbon olefins, 1-butene, 2-butenes, and isobutene, have been investigated over numerous catalyst systems. The majority of these catalysts are of the same types used in the oxidation of propylene. In general, the oxidation of the four carbon olefins is less selective than propylene oxidations. The nature of the products produced is a function of the catalysts used and the structure of the olefin. For example, in the oxidation of the n-butenes over group I mild oxidation catalysts, two types of products are produced. Over bismuth-molybdate catalysts, the n-butenes are converted selectively to 1,3-butadienes, while cuprous oxide catalysts produce unsaturated aldehydes and ketones. Strong oxidation catalysts, such as group II acrylic acid catalysts, oxidize the n-butenes to maleic anhydride. The behavior of isobutene on oxidation is very similar to that of propylene. Over mild oxidation catalysts methacrolein is produced, while methacrylic acid is obtained over stronger oxidation catalysts.

The oxidation of n-butenes over bismuth molybdate catalysts...
has been the subject of numerous investigations. Over these catalysts, oxidative dehydrogenation occurs to produce 1,3-butadiene very selectively even at high n-butene conversions. Adams and co-workers\textsuperscript{35} reported that at 460°C, butadiene was produced in 90% selectivity at 80-90% 1-butene conversion. The 2-butenes are less reactive than 1-butene; the trans isomer was found to be only 0.19 as reactive relative to 1-butene, while cis-2-butene is slightly more reactive at 0.26 relative to 1-butene\textsuperscript{33,34}. Along with butadiene, a number of by-products are formed, including 2-butenes, furan, maleic anhydride, acrolein, acetaldehyde, formaldehyde, acetone, methyl ethyl ketone, methyl isopropyl ketone, malonic, acetic, and formic acids\textsuperscript{33,35-36}.

In an attempt to determine the reason for the differences in the oxidation of propylene and n-butenes over bismuth-molybdenum (why propylene is oxidized to an unsaturated aldehyde and n-butenes to butadiene) Serebryakov and co-workers\textsuperscript{36}, determined the activation energies for the formation of various products during oxidation of 1-butene. The activation energies (keal/mole) are: butadiene 13, butene isomers 4.5, maleic anhydride 24, acrolein 25, \( \text{CO}_2 \) 35, and acetaldehyde 27. Thus over bismuth molybdate catalysts, the oxidative dehydrogenation of n-butene is favored over oxidation to a carbonyl compound. It is well accepted, that at temperatures of 400-500°C, at which most catalytic oxidations occur, oxidative dehydrogenation will predominate over the oxidation to carbonyl compounds when permitted by the olefin structure. Thus, propylene
is converted into acrolein over bismuth molybdate catalysts since its structure prohibits the formation of a diene.

Numerous catalyst systems have been found useful for the conversion of the n-butenes to 1,3-butadiene. The majority of these catalyst systems are of the same type used for the mild oxidation of propylene, i.e., group I catalysts, excluding cuprous oxide catalysts. Of the catalysts that have been used, most are based on bismuth and molybdenum in which various additives have been incorporated to improve the selectivity of the dehydrogenation. Next to the bismuth molybdates, antimony oxide containing catalysts are the most commonly used. A number of antimony oxide containing catalysts have been investigated in which the second metal is one of the following: V, Fe, Cr, Sn, Ni, U, Mn, and Co. The most selective catalyst system was an antimony-iron oxide while the most active was an antimony-vanadium oxide. Other catalyst systems have been used in the oxidative dehydrogenation of n-butenes, including a calcium-nickel-chromium phosphate, acidic chromia-alumina, and various ferrite-based catalysts.

Over cuprous oxide catalysts, n-butenes undergo oxidation to unsaturated aldehydes and ketones rather than dehydrogenation to butadiene. Hearne and Adams, showed that over a cuprous oxide catalyst, 1-butene and 2-butene are oxidized to methyl vinyl ketone. The oxidation of n-butenes over a silice supported cuprous oxide catalyst has been studied by a number of workers. In the presence of this catalyst, the oxidation of 1-butene and 2-butene
proceeds with a higher activation energy than the oxidation of propylene (18 kcal/mole for n-butenes and 12-13 kcal/mole propylene) and yields a more diverse mixture of reaction products. At a n-butene:oxygen:nitrogen molar ratio of 40:10:50 and a contact time of 0.45 seconds, the following products were observed: methyl vinyl ketone (50-63% formed), crotonaldehyde (8-16%), acetone (2-17%), methyl ethyl ketone (2-12%), acrolein (3-9%), methyl vinyl carbinol (2-6%), 1,2-epoxybutane (0.4-5%), 2,3-epoxybutane (0.3-4%), butyraldehyde (2-4%), 1,3-butadiene (1-3%), and propionaldehyde (0.7-9%). The yield of methyl vinyl ketone was higher from 1-butene.

Cuprous oxide is not the only known catalyst for the oxidation of n-butenes to unsaturated ketones and aldehydes. For example Clark and Shutt 47 have shown that metal selenite and tellurite catalysts oxidize 1-butene to methyl vinyl ketone and 2-butene to crotonaldehyde. Tan and co-workers 48 reported the formation of methyl ethyl ketone from n-butenes over tin-molybdenum and cobalt molybdenum catalysts at low temperatures (less than 500°C). At 135°C and in the presence of 9:1 SnO₂MoO₃ catalyst, a yield of 85.5% was observed for methyl ethyl ketone at a 1-butene conversion of 5%. As the temperature increased the yield fell to 24.7% at 210°C with a 1-butene conversion of 17.5%. In the oxidation of 2-butene over the same catalyst, 61% of methyl ethyl ketone was formed at a 2-butene conversion of 4% along with significant amounts of acetaldehyde (15%) and acetic acid (18%). Over the 9:1 Co₅O₄MoO₃
catalyst, the butenes were oxidized less selectively and more slowly than over the tin containing catalysts. For example, 2-butene was converted to methyl ethyl ketone (26.7% yield) at 233°C, declining to 14.3% at 270°C with 2-butene conversions of 2.5% and 6.7%, respectively. The 1-butene isomer yield 60.8% of the ketone at 240°C, decreasing to 27.8% at 274°C with 1-butene conversions of 2.2% and 5.2% respectively.

The oxidation of the n-butenes over "strong" oxidation catalysts, such as a group II acrylic acid catalyst or a vanadium oxide based catalyst, results in the production of maleic anhydride. In the oxidation of cis-2-butene over a $\text{V}_2\text{O}_5$-$\text{P}_2\text{O}_5$ (1:1.6 atomic ratio) on pumice catalyst at 550°C, Ai reported a selectivity toward maleic anhydride of 42% at a cis-2-butene conversion of 92%. In the absence of phosphorus, the selectivity to maleic anhydride fell to 20% at a cis-2-butene conversion of 70%. According to Ai, the beneficial action of $\text{P}_2\text{O}_5$ is the result of suppressing further oxidation of maleic anhydride. For example, at 500°C on pure $\text{V}_2\text{O}_5$, 25% of the maleic anhydride formed under went complete oxidation, while only 2% was further oxidized on a $\text{P}_2\text{O}_5$ containing catalyst. Bissot and Benson reported that cis-2-butene was converted to maleic anhydride at a yield of 55% and a cis-2-butene conversion of 92% over a cobalt molybdate catalyst at 150-475°C. The 2-butenes are generally less reactive than 1-butene. However at 400°C, Avietsov and co-workers reported that the conversion values were very similar.
In addition to maleic anhydride, a number of other products are obtained in the oxidation of the n-butenes to maleic anhydride. These include n-butene isomers, butadiene, furan, carbon oxides, water, acetaldehyde, formaldehyde, acrolein, crotonaldehyde, formic acid, acetic acid, and methyl vinyl ketone\(^{53-55}\). Butadiene, crotonaldehyde, and furan are generally considered the key intermediates in the reaction pathway to maleic anhydride. To gain further insight into the pathway of the oxidation of the n-butenes, various workers have carried out the oxidation of butadiene, crotonaldehyde, and furan over these catalysts and have studied the effect of the variation of contact time in n-butene oxidations. Based upon these studies, the following reaction pathway can be proposed:

\[
\text{butenes} \rightarrow \text{butadiene} \rightarrow \text{crotonaldehyde} \rightarrow \text{furan} \rightarrow \text{maleic anhydride} \downarrow \text{crotonic acid} \]

Due to the variety of catalysts and reaction conditions employed, exceptions in the oxidation of the n-butenes to maleic anhydride have been noted. For example, Ostroushko and others\(^{55}\) suggested that in the presence of \(\text{V}_2\text{O}_5-\text{P}_2\text{O}_5\) catalysts, maleic anhydride can be formed from crotonaldehyde, omitting the furan stage. This is believed to occur by the oxidation of crotonaldehyde to crotonic acid which is further oxidized to maleic anhydride with the possible intermediate formation of 4-hydroxy-2-butenoic acid lactone\(^{55,56-59}\). According to Delgrange and Blanchard\(^{58}\), maleic anhydride is obtained from crotonaldehyde only through the furan stage over a \(\text{V}_2\text{O}_5-\text{MoO}_3\)
catalyst. Furthermore, Ai suggests that the oxidation of furan is the principal step in determining the rate of formation of maleic anhydride and the selectivity of the process. Although it appears that the reaction pathway is unclear after crotonaldehyde is formed, it is agreed that butadiene is formed initially and is then oxidized to crotonaldehyde.

Isobutene is selectively oxidized over catalysts employed in the oxidation of propylene to yield methacrolein and methacrylic acid. The structure of isobutene prohibits the formation of a diene by dehydrogenation so an allylic oxidation occurs, in which an allylic methyl group is oxidized to an aldehyde or carboxylic acid function. Group I acrylic acid catalysts are commonly employed to produce methacrolein. Popova and co-workers have reported that over a copper oxide catalyst, methacrolein was produced in yields of 72%. The addition of small amounts of gaseous additives such as selenium dioxide, sulfur dioxide, and various halogenated hydrocarbons have been shown to increase the selectivity of methacrolein in the oxidation of isobutene over copper oxide catalysts.

For example, in the oxidation of isobutene over a copper catalyst at 400°C with an isobutene-oxygen-nitrogen ratio of 0.11:0.11:0.41 (moles/hr), methacrolein was produced in a yield of 24.8% at an isobutene conversion of 20.1%. Upon addition of a small amount of tetrachloroethylene, the yield of methacrolein increased to 80.3% at an isobutene conversion of 37.9%. This increase in selectivity over copper oxide has been attributed to the ability of the modifier
to suppress the further oxidation of methacrolein.

Bismuth molybdates are also useful catalysts for the oxidation of isobutene to methacrolein. Adams\textsuperscript{64} showed that over a Bi-Mo catalyst at 460°C and an isobutene conversion of 70%, a 72% yield of methacrolein is produced. Malinowski\textsuperscript{65} concluded that the optimum conditions for the oxidation over a bismuth molybdate catalyst occurs with a catalyst consisting of Bi$_2$O$_3$·2MoO$_3$ and an isobutene-oxygen-steam mixture 1:1.9:4.5. This resulted in a 92.1% selectivity to methacrolein at 88.9% conversion of isobutene. A number of other catalyst systems similar to those used in the oxidation of propylene to acrolein have also been investigated.

In addition to methacrolein, a number of other products are often produced. Such products usually include acrolein, propion-aldehyde, acetaldehyde, formaldehyde, carbon oxides, and water.

Isobutene can also be oxidized to methacrylic acid over catalysts and conditions similar to those used for the oxidation of propylene to acrylic acid. Direct oxidation of isobutene to methacrylic acid usually results in a mixture of the aldehyde and acid. For example, Isaev and Margolis\textsuperscript{24} reported that over a Co$_6$Mo$_{12}$Bi$_{0.5}$Fe$_{0.5}$-1.0$^0_x$ catalyst at 380°C and a contact time of 3.6 seconds, a mixture of 5 volume % isobutene, 65% air, and 30% steam resulted in an isobutene conversion of 95% with methacrylic acid and methacrolein yields of 17-19% and 55-60%, respectively.

Oxidation of C$_5$ Olefins

The oxidation of five carbon olefins over common oxidation
catalysts proceeds much less selectively than in the case of the three and four carbon olefins. Once again, the selectivity and the types of products obtained are a function of the structure of the olefin and the types of catalysts employed.

The five carbon monolefins can be divided into two groups: the straight chain or normal pentenes (1-pentene, cis- and trans-2-pentenes) and the branched chain or isopentenes (2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene). Over mild oxidation catalysts such as cuprous oxides and bismuth molybdates, the n-pentenes undergo oxidation to various aldehydes and ketones and oxidative dehydrogenation to pentadienes. Over a stronger oxidation catalyst such as vanadium pentoxide, the n-pentenes are converted to a variety of oxygenated compounds including aldehydes, ketones, acids, epoxides, anhydrides, alcohols, and lower olefins. Under these conditions, no pentadienes are produced. Similarly, the isopentenes undergo oxidation to unsaturated aldehydes and ketones, and dehydrogenation to isoprene (2-methyl-1,3-butadiene) over cuprous oxides and bismuth molybdates. A number of oxygenated products are obtained from the oxidation of the isopentenes over a vanadium pentoxide catalyst.

The oxidation of the diolefin, 1,5-pentadiene (piperylene) has been investigated over a number of catalysts. Over a mild oxidation catalyst, 2,4-pentadienal is observed while the use of stronger oxidation catalysts lead to 2-furaldehyde or maleic anhydride.
Gorokhovatskii and co-workers\textsuperscript{66} showed that over a cuprous oxide catalyst supported on carborundum at temperatures between 280 and 360°C and residence times of 0.15 to 1.6 seconds, a mixture of 1-pentene and 2-pentene (59:41 v/v) was oxidized to a variety of products. The main products consisted of 2-penten-4-one, ethyl vinyl ketone, propionaldehyde, acrolein, 2,4-pentadienal, and 1,3- and 2,3-pentadienes. Small amounts of 2-pentenal and trace amounts of all other normal five carbon unsaturated aldehydes and ketones, C\textsubscript{1}-C\textsubscript{5} saturated aldehydes, 4-butenal, acetone, methyl ethyl ketone, and methyl propyl ketone were also observed. In the oxidation of 1-pentene, the yields of ethyl vinyl ketone, propionaldehyde, and acrolein were considerably higher.

Over bismuth molybdates at 400°C, Adams\textsuperscript{35} reported that the predominant reaction of the \textit{n}-pentenes was the oxidative dehydrogenation to piperylene. Unlike the dehydrogenation of 1-butene, the selectivity to piperylene rapidly diminishes with increasing conversion of 1-pentene. For example, at a 1-pentene conversion of 10\%, a selectivity toward piperylene of 95\% was observed, falling to 38\% at 60\% conversion of 1-pentene. According to Adams\textsuperscript{64}, this is a common feature of bismuth molybdate catalyzed oxidation of olefins higher than the butenes. The explanation for this behavior involves the inhibition of the reaction by the product piperylene. Adams attributes this inhibition to the interference of the inhibitor with oxygen chemisorption which controls the rate determining step of the reaction; the abstraction of an allylic hydrogen from a gas-phase
or physisorbed olefin by strongly chemisorbed oxygen atoms.

Butt and Fish \textsuperscript{67} have investigated the oxidation of the n-
pentenes over a "strong" oxidation catalyst, a pumice supported
vanadium pentoxide. Over this catalyst, cis- and trans-2-pentenes
behave identically while the oxidation of 1-pentene proceeds largely
via isomerization to 2-pentene followed by oxidation of the latter.
The activity and selectivity of the reaction is strongly dependent
upon the life of the catalyst. After about five hours of use, the
catalyst showed vastly different behavior. The oxidation becomes
more rapid but much less selective yielding at least fourteen
additional products.

The oxidation of 2-pentene on a "new" catalyst (one with less
than five hours of use) at 300°C and a contact time of 30 seconds
(based on total surface area of the catalyst) resulted in the forma-
tion of acetaldehyde (major product), propionaldehyde, acetone,
ethylene, propylene, trans-2,3-epoxypentane, 1-pentene, and carbon
dioxide. After five hours of use, additional products such as
methanol (in large amounts), ethylene oxide, propylene oxide, 5-
methylbutan-2-one, 2-methyl-2,3-epoxypropane, trans-2,3-epoxybutane,
2-pentanone, 3-pentanone, crotonaldehyde, butanone, ethanol,
2-butanol, maleic acid, crotonic acid, and citraconic acid were also
produced.

This unusual behavior is attributed to a change in the mecha-
nism of the oxidation as a result of a modification of the catalyst
during the oxidation. On a new catalyst, the oxidation occurs in
the absence of oxygen indicating that the oxidant is lattice oxygen of the catalyst (a common feature of many heterogeneous oxidation catalysts). During the oxidation, the "new" catalyst which is predominantly pentavalent vanadium is gradually reduced to tetravalent vanadium. When the latter attains a critical concentration, a phase change occurs resulting from a reaction of the vanadium oxides with the pumice support (which contains sodium) to give sodium vanadyl vanadate. Over this phase, the oxidation will not occur in the absence of oxygen indicating that molecular oxygen is now the active oxidant. Under these conditions, the reaction acquires a free radical-chain character which results in the increased activity and loss of selectivity.

In the presence of cuprous oxide catalysts, the isopentenes are either oxidized to carbonyl compounds, dehydrogenated to isoprene, or both, depending upon the reaction conditions and the isomer undergoing oxidation. Belen'kii et al. and Radzhabli and co-workers have investigated the reactivity of the isopentenes towards oxidation and dehydrogenation. In oxidative dehydrogenation, the following order of reactivity was observed:

3-methyl-1-butene > 2-methyl-1-butene > 2-methyl-2-butene

while the reactivity toward oxidation to carbonyl compounds was:

2-methyl-1-butene > 2-methyl-1-butene > 3-methyl-1-butene.

Gorokhovatskii and co-workers have investigated the oxidation of mixtures of the isopentenes (3-methyl-1-butene:2-methyl-1-butene:2-methyl-2-butene ratios of 8:16:76 and 95:5:5:5) over a cuprous
oxide catalyst at temperatures between 314 and 361°C. The main products were carbon dioxide, isoprene, acetone, 2-ethyl propenal, and 3-methyl-3-butene-2-one. Small amounts of acrolein, methylketene, 2-methyl-3-butenal, and 3-methyl-2-butenal, and 2-methyl-2-butenal also formed. It was thought that 2-ethyl propenal and 3-methyl-3-butene-2-one were probably formed from 2-methyl-1-butene and 2-methyl-2-butene, while 3-methyl-2-butenal was formed from both 3-methyl-1-butene and 2-methyl-2-butene.

Over bismuth molybdates, the isopentenes undergo isomerization, oxidative dehydrogenation, and oxidation to unsaturated aldehydes. According to Adams, over bismuth molybdate at 460°C, 3-methyl-1-butene is oxidized to isoprene and 2-methylene-3-butenal. Under similar conditions, isoprene, 2-methyl-2-butenal, 3-methyl-2-butenal, and 2-methylene-3-butenal was obtained from 2-methyl-2-butene. The oxidation of 2-methyl-1-butene produced isoprene, 2-methylene-3-butenal, and 2-ethyl propenal. The following reaction scheme (in Figure 1) can be envisioned for the oxidation of the isopentenes on bismuth molybdate.

According to Adams, isoprene is formed at a much faster rate than unsaturated aldehydes from the isopentenes. Furthermore, a branched allylic methyl group appears to be necessary for aldehyde formation. It is also interesting that no unsaturated ketones have been found from the oxidation over bismuth molybdate, although they are formed over cuprous oxide.

Adams has shown that like the oxidation of the n-pentenes over
Figure 1. Reaction scheme for the oxidation of the isonentenes on bismuth molybdate.
bismuth molybdate, inhibition by the reaction products also occurs in the oxidation of the isopentenes. This inhibition is more severe in the case of the isopentenes due to the type of products obtained (isoprene and aldehydes). The aldehydes produced are much more strongly adsorbed (roughly two orders of magnitude) than the diene, resulting in a greater degree of inhibition. Thus, 3-methyl-1-butene which produces only isoprene as the initial product is only moderately inhibited while 2-methyl-1-butene which produces a small amount of unsaturated aldehyde as initial products, is severely inhibited and the selectivity is reduced substantially. At conditions where the 2-methyl-1-butene conversion would be expected to be 80%, the actual conversion is only 6%.

In the presence of the "strong" oxidation catalyst, vanadium pentoxide, Butt and Fish have shown that the isopentenes undergo oxidation and isomerization. Over a pumice supported vanadium pentoxide catalyst at a temperature range of 200 to 400°C with a contact time of 33.6 seconds (based upon the total surface area of the catalyst), the isopentenes isomerize to 2-methyl-2-butene followed by the oxidation of the latter. The main products formed are characteristic of oxygen addition at the double bond and subsequent cleavage of that bond. Above 240°C, the main products were acetaldehyde, acetone, 3-methylbutan-2-one, 2,3-epoxy-2-methylbutane, with small amounts of propylene, ethylene, butanone, n-hutyraldehyde, and unspecified C_{10} hydrocarbons. The highest yields of acetaldehyde (62.5%) and acetone (45.5%) were obtained at 350°C, whereas the
highest yield of 2,3-epoxy-2-methylbutane occurred at 300°C. Unlike the oxidation of the n-pentenes at similar conditions, the nature of the isopentene oxidation does not change significantly with catalyst age. Over this catalyst, the mechanism appears to involve lattice oxygen as the active oxidant.

Popova and others have reported that over copper oxide catalysts containing the oxides of certain heavy metals, piperylene could be selectively oxidized to 2,4-pentadienal. The oxidations were conducted in the temperature range of 400-410°C and contact times between 0.9 and 2.0 seconds in the presence of silit supported copper oxide catalysts with or without additives. Over a pure copper oxide catalyst (0.3% CuO content), the selectivity to 2,4-pentadienal was low (35.1% at piperylene conversions of 5.4%). With the addition of molybdenum to the catalyst, the selectivity increased to 57.7% at a conversion of 9.7%. The best catalyst system studied was that of a 1.5% copper oxide with added molybdenum and tungsten oxides (1-2% of the copper oxide content). Over this catalyst at a contact time of 2.0 seconds, a mixture of piperylene, oxygen, and nitrogen (1:1.6:1.84) resulted in a piperylene conversion of 10.3%, at a 2,4-pentadienal yield of 65.2%. The optimum reaction conditions over this catalyst were found to be at a temperature range of 400 to 410°C, a contact time of 0.9 seconds, and a feed gas composition of 15-20% piperylene, 25% oxygen, and 60-55% nitrogen. At these conditions, a maximum yield of the aldehyde approached 75%, with the remaining by-products consisting of acetaldehyde, carbon dioxide and...
According to Popova et al.\textsuperscript{73-74}, the selective oxidation of piperylene to 2,4-pentadienal occurs over a copper catalyst containing both cupric and cuprous oxides. The diene is thought to be adsorbed on cuprous oxide via the allylic methyl group and undergoes oxidation to the dienal. The competing reaction, in which the diene is adsorbed at one of the double bonds, occurs on cupric oxide and results in complete combustion to carbon dioxide and water. The addition of the oxides of molybdenum and tungsten is believed to improve the selectivity by increasing the energy of activation for the formation of carbon dioxide. The role of the heavy metal oxides is believed to function by blocking the more energetically active sections of the cupric oxide surface formed during preparation of the catalyst. The addition of the additives fails to affect the formation of the dienal since it proceeds on cuprous oxide which is formed during the time of the catalytic reaction itself.

In the presence of a catalyst containing oxides of molybdenum, copper, arsenic, and tellurium (25:8:4:1) supported on silicon carbide (5.5 wt %), Vrchoski and Sheeham\textsuperscript{75} have shown that piperylene is oxidized to 2-furaldehyde. Over this catalyst at 485°C, a contact time of 7.2 seconds, and a feed containing 7.5 volume % piperylene, 20.9% oxygen, 28.8% nitrogen and 45% steam, 2-furaldehyde was obtained at a selectivity of 26.5 wt %. Yonamato and co-workers\textsuperscript{76} have reported that over a vanadium molybdate catalyst, piperylene, cyclopentene, 1-pentene, and a five
carbon fraction of cracked naptha was oxidized to maleic anhydride. The maximum yields obtained at optimum reaction conditions, from piperylene, cyclopentene, 1-pentene, and the five carbon naphtha cut, were 35, 40, 15, and 29 mole % respectively. Subsequently, Ikawa et al. have obtained a patent on the use of vanadium molybdate catalysts (7:3 V₂O₅-MoO₃) for the oxidation of piperylene or a piperylene rich feed to maleic anhydride. When a feed of air and 1% hydrocarbon fraction containing 48% piperylene, 6% cyclopentadiene, 9% cyclopentene, and 54% paraffins was passed over such a catalyst at a temperature less than 440°C, a 43% yield of maleic anhydride was obtained. Another patent has been issued for the oxidation of piperylene to maleic anhydride. This patent describes the use of a catalyst containing oxides of vanadium, phosphorus, and lithium (1.5 P and 0.5 Li per V).

Finally Krylova and co-workers have reported a study in which oxygen containing compounds formed during the catalytic oxidation of piperylene to maleic anhydride were identified by mass spectroscopy and gas chromatography. Some of the by-products identified include citraconic, dimethylmaleic, and phthalic acids, α-indenone, cinnamaldehyde, methyl cinnamaldehyde, phthalide, coumarin, methyl coumarin, isocoumarin, benzophenone, fluorenone, methylfluorenone, and anthraquinone.
EXPERIMENTAL

Oxidation Apparatus

The oxidation apparatus consisted generally of a vaporizer-preheater section, a tubular reactor, and a product recovery and separation section. A diagram of this apparatus is shown in Figure 2.

The vaporizer-preheater section, which consisted of a two stage steam generator and a preheater element, was constructed of 1/4 inch diameter 316 stainless steel tubing. The steam generator was made up of a vertically mounted eight inch section of tubing (stage one) attached to a seven inch section (stage two) via a 316 stainless steel "T" connector (Swagelok). To the other end of the "T" was connected a pressure gauge (Mastergauge Type 100-M-monel, Marsh Instrument Company). Water from a syringe pump was fed to a water injector located in the steam generator (stage one) via a 1/8 inch teflon line. The injector consisted of a three inch section of 1/8 inch stainless steel tubing to which one end was connected a 1 1/2 inch long hypodermic needle (gauge 25). This end was connected to the steam generator (stage one) by a 1/8 inch to 1/4 inch stainless steel connector (Swagelok). The other end of the injector was attached to the teflon line from the syringe pump. The purpose of this injector was to minimize flash vaporization effects of the steam generator. The two sections of the steam generator were electrically heated by #20 asbestos insulated nichrome wire. Each section of the steam generator was wrapped with the nichrome wire
Figure 2. Oxidation Apparatus
over a layer of asbestos tape followed by more tape, a second layer of wire, and insulated with approximately 1 1/2 inches of asbestos cloth.

The outlet of the steam generator (stage two) lead into a stainless steel "T" connector which was attached to the preheater section. The preheater consisted of a five inch length of tubing which was heated by nichrome wire similarly to that of the steam generator. The other end of the "T" was the inlet for the air and vaporized hydrocarbon feed.

Air was introduced through a Kendall Model 10 pressure regulator to a Kontes 2C-G-6 rotometer. The exit of the rotometer lead to a 316 stainless steel "T" connector which served as the vaporizer for the hydrocarbon feed. The hydrocarbon feed was delivered to the "T" connector from a syringe pump via a 1/8 inch teflon line. The "T" was maintained at 25°C with an electrical heating tape. The exit of this "T" connector lead to the inlet of the preheater.

The temperature of each section of the vaporizer-preheater was monitored with thermocouples. The thermocouples were placed in thermowells constructed of 1/8 inch copper tubing and placed between the 1/4 inch tubing and the first layer of asbestos tape.

The syringe pumps employed for the delivery of water and hydrocarbon feed were Stage Instruments model 355 variable flow syringe pumps. Hamilton Gas-Tite glass syringes with Teflon-coated plungers were used for the hydrocarbon feed (50 cc) and water (20 cc).

The reactor consisted of a four inch length of 0.303 inch
inner diameter 304 stainless steel threaded pipe. The reactor was mounted in the center of a furnace and the inlet and exit of the reactor was extended to the ends of the furnace by means of two 5 inch lengths of 1/4 inch diameter stainless steel tubing attached to the reactor by means of reducing adapters (Swagelok). The outlet extension was attached to the reactor exit line which consisted of a seven inch section of 1/4 inch diameter stainless steel tubing. The exit line which lead to the scrubber was heated in the same manner as the vaporizer-preheater and the temperature was also monitored by a thermocouple. The reactor heating was accomplished and controlled by a Lindberge Single-Zone 1010°C tube furnace (model 54051) equipped with a solid state digital temperature controller (type 2200, model 59344). The thermocouple detecting element of the controller was repositioned to the outside surface of the reactor for improved temperature control. When required, the heat of reaction was removed by a flow of air provided by a 1/4 inch copper line mounted in the exit end of the furnace.

Temperature monitoring of the reactor was accomplished with aid of three thermocouples attached to the outside of the reactor tube by means of asbestos tape.

In the product recovery and separation section, a water scrubber, consisting of a ten inch length of 5/4 inch diameter pyrex tubing closed at one end and attached to a 19/22 three-way connecting tube, was immersed in a water bath which was heated by a GCA/Precision Scientific Porta Temp immersion heater. The bath
temperature was maintained at 45°C to ensure that any C₅ or lower hydrocarbons would not condense in the scrubber. The inlet of the scrubber consisted of a 13 inch section of 1/8 inch stainless steel tubing fitted in a #2 rubber stopper which extended into the scrubber and was attached to the reactor exit line by way of a 90° connector. The exit of the scrubber consisted of a 12 inch section of 1/4 inch diameter tygon tubing fitted to a #2 rubber stopper and leading to a septum in which samples were drawn for the analysis of the hydrocarbon stream. From the septum a four inch section of 1/4 inch tygon tubing lead to a 50 ml filter flask packed with four millimeter diameter glass beads. This flask served to condense any remaining water vapor in the hydrocarbon stream. The exit of this trap lead to the hydrocarbon trap via a eight inch length of 1/4 inch tygon tubing.

The hydrocarbon trap consisted of a 65 inch section of 1/4 inch diameter copper tubing which was coiled to a diameter of three inches. One end of this tubing was attached to a copper "T" connector (Swagelok) while the other end was connected to the exit of the filter flask. Another end of the "T" connector was attached to a one inch section of 1/4 inch copper tubing which was inserted in a #1 rubber stopper fitted to a 25 ml Erlenmeyer flask. The remaining end of the "T" was attached to a seven inch length of 1/4 inch copper tubing which served as the exit. This trap was mounted in a Dewar flask containing ethanol which was maintained at -80°C by a refrigeration unit (FTS Systems, Inc.). The exit of the trap lead
to a septum, where samples were drawn for carbon dioxide analysis, via a six inch section of 1/4 inch tygon tubing. The other end of the septum exited into a hood.

Total gas flow of the hydrocarbon stream and carbon dioxide stream was determined by a GCA/Precision Scientific wet test meter inserted in the gas streams after the sample ports. This necessitated the sampling of one stream at a time while its flow rate was measured and repositioning of the wet test meter for sampling of the other stream.

All thermocouples utilized were Type J (iron-constantan) and temperature monitoring was accomplished with a Fluke 2100A 10-Channel Digital Thermometer.

Power for the various heating elements was supplied by individual variable transformers.

Analytical

Analysis of all reaction products was performed by gas chromatography. The oxygenated products (those products collected by the water scrubber) were analyzed on a six foot length of 1/8 inch outside diameter stainless steel tubing packed with 10% SP-1200 (Supelco, Incorporated) and 1% H₃PO₄ on acid-washed Chromosorb W, 80/100 mesh. The column was mounted in a Hewlett-Packard model 5710A gas chromatograph equipped with a flame-ionization detector, a 5706A dual differential electrometer, and a Linear Instruments integrating chart recorder (model 252A/mm). The column was initially conditioned for one day at 195°C with a helium carrier flow rate of
20 ml per minute.

Analysis of the oxygenated product samples were carried out using a temperature program which initially held the G.C. column at 60°C for a period of four minutes, then increased the temperature at a rate of 8°C per minute to 180°C, this temperature being maintained until all peaks had eluted. The injector temperature was 250°C and the detector 300°C. A helium gas flow of 20 ml per minute, hydrogen flow of 20 ml per minute, and air flow of 80 ml per minute were utilized.

Analysis of the aqueous solution from the scrubber (oxygenated products) lead to severe ghosting problems. To eliminate this difficulty an extraction procedure was employed in preparing samples of the oxygenated products. At the end of a run, the solution in the scrubber was diluted to 25.00 ml and added to a 60 ml separatory funnel. One 2.00 ml portion of dichloromethane was added to the funnel, shaken, dichloromethane layer removed, and diluted to 2.00 ml. A 1.00 µl sample of this solution was used for the analysis and was taken with a Hamilton 701-10K 10 µl glass syringe. After each sample introduction, the syringe was rinsed repeatedly with dichloromethane and cleaned with a Hamilton syringe cleaner (Model 76610).

Typically, the oxygenated product samples acquired during a run produced a large number of peaks. The diverse number of peaks encountered in the various oxidation runs are given in Table I. Comparisons of the retention times for various standards with this data and the use of internal standards lead to the peak identities
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<tr>
<td>21</td>
<td>11.35</td>
<td>variable</td>
<td>44</td>
<td>24.10</td>
<td>trace</td>
</tr>
<tr>
<td>22</td>
<td>11.55</td>
<td>major</td>
<td>45</td>
<td>25.60</td>
<td>trace</td>
</tr>
<tr>
<td>23</td>
<td>11.90</td>
<td>variable</td>
<td>46</td>
<td>26.45</td>
<td>trace</td>
</tr>
</tbody>
</table>
in Table II. A sample of 2,4-pentadienoic acid was prepared by a modification of the procedure presented by Glushkov and Magidson. The 2,4-pentadienal standard was synthesized by a modification of the procedure developed by Woods and Sanders.

Standard samples of 2,4-pentadienal for the construction of a calibration curve for the conversion of chromatogram peak area to molar quantities were prepared in the following manner: aqueous solutions of 2,4-pentadienal at various concentrations, stabilized with 0.40% hydroquinone, were extracted and chromatographed by the method previously described for the oxygenated samples. Linear regression analysis of the calibration data yielded a straight line, with a correlation coefficient greater than 0.99.

To maintain the response of the flame-ionization detector, so that, the calibration curve was not affected, standard samples of chlorobenzene were used to provide a reference for detector response adjustment.

Analysis of the hydrocarbon stream was accomplished on a 25 foot length of 1/8 inch outside diameter stainless steel tubing packed with 15% 8,8'-Oxydipropionitrile (Supelco, Incorporated) on acid-washed Chromasorb W, 80/100 mesh. The column was mounted in a Hewlett-Packard model 5710A gas chromatograph. The column was initially conditioned at 70°C for two days at a helium carrier flow rate of 50 ml per minute.

The hydrocarbon samples were analyzed at 25°C with an injector temperature of 25°C and detector temperature of 200°C. A helium gas
TABLE II

Peak Identities for Oxygenated Reaction Products

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>2,4-pentadienal</td>
</tr>
<tr>
<td>15</td>
<td>2-furaldehyde</td>
</tr>
<tr>
<td>20</td>
<td>acrylic acid</td>
</tr>
<tr>
<td>50</td>
<td>2,4-pentadienoic acid</td>
</tr>
</tbody>
</table>
flow of 20 ml per minute, hydrogen flow of 20 ml per minute and air
flow of 80 ml per minute were utilized.

Sample sizes of 0.50 cc were used and were taken with a Stylex
Tuberculin 1.00 cc syringe. Typically, the samples taken during an
oxidation run produced a series of peaks given in Table III.
Comparison of the retention times for various standards with this
data and the use of internal standards lead to the peak identities
given in Table IV.

For the conversion of chromatogram peak areas to molar
quantities, standard mixed samples of 2-methyl-2-butene (Eastman),
cyclopentene (J. T. Baker), cis-1,3-pentadiene (Fluka AG, Buch SG),
and trans-1,3-pentadiene (Aldrich) were prepared as follows: the
desired quantities of liquid samples of the four hydrocarbons were
injected into a gas sample flask (158.8 ml) fitted with a rubber
septum which had previously been flushed with air. Vaporization and
mixing were facilitated by a stirring bar previously placed in the
gas sample flask.

Standard samples of cyclopentene vapor were utilized as a
reference for detector adjustment to maintain the response of the
flame-ionization detector so that the calibration curves were not
affected.

Analysis of the piperylene feed material using the described
method gave the following results shown in Table V.

Analysis for carbon dioxide was performed on a 50 foot 22%
Bis (2-Ethoxyethyl) Sebacate & 8% Bis (2-Ethoxyethyl) Adipate on
### TABLE III

Peak Retention Times for Hydrocarbon Stream

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Retention Time (min)</th>
<th>Peak Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.60</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>6.40</td>
<td>variable</td>
</tr>
<tr>
<td>3</td>
<td>7.01</td>
<td>minor</td>
</tr>
<tr>
<td>4</td>
<td>9.23</td>
<td>major</td>
</tr>
<tr>
<td>5</td>
<td>10.89</td>
<td>major</td>
</tr>
<tr>
<td>6</td>
<td>12.12</td>
<td>major</td>
</tr>
<tr>
<td>7</td>
<td>16.38</td>
<td>variable</td>
</tr>
</tbody>
</table>

### TABLE IV

Peak Identities for Hydrocarbon Stream

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>2-methyl-2-butene</td>
</tr>
<tr>
<td>4</td>
<td>cyclopentene</td>
</tr>
<tr>
<td>5</td>
<td>trans-1,3-pentadiene</td>
</tr>
<tr>
<td>6</td>
<td>cis-1,3-pentadiene</td>
</tr>
<tr>
<td>7</td>
<td>--</td>
</tr>
</tbody>
</table>
### TABLE V

Composition of Piperylene Feed

<table>
<thead>
<tr>
<th>Component</th>
<th>% Composition (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl-2-butene</td>
<td>1.8%</td>
</tr>
<tr>
<td>cyclopentene</td>
<td>16.1%</td>
</tr>
<tr>
<td>trans-1,5-pentadiene</td>
<td>69.5%</td>
</tr>
<tr>
<td>cis-1,5-pentadiene</td>
<td>12.6%</td>
</tr>
</tbody>
</table>
Chromosorb P, 45/60 mesh, 1/8 inch stainless steel column. The column was mounted in a Sargent Thermal Conductivity gas chromatograph, model A9231, equipped with a Linear Instruments integrating chart recorder (model 252A/mm). The column was conditioned at 150°C for two days. A helium carrier gas flow of 11 ml per minute was used. A column temperature of 35°C was used with an injector temperature of 65°C and a detector temperature of 70°C.

Carbon dioxide samples of 0.50 cc size were utilized in the analysis and were taken with a Stylex Tuberculin 1.00 cc syringe. Standard samples of carbon dioxide used in the preparation of a calibration curve were prepared in the following manner: a gas sample bottle fitted with a rubber septum was flushed with air and sealed. A volume of gas equal to the quantity of carbon dioxide standard (Airco, Inc., 99%) to be used was withdrawn from the sample bottle, followed by injection of the standard into the bottle via a Hamilton Gas-Tite syringe. Mixing was performed by a stirring bar previously placed in the sample bottle.

To maintain the response of the thermal conductivity detector, so that, the calibration curve was not affected, 0.50 cc samples of air were used to provide a reference for detector response adjustments.

Catalyst Preparation

The supported catalysts utilized in this project were prepared by the incipient wetness method, which provides that the active metals are deposited in the pores of the supports for maximum surface
area. In this method, metal salts are dissolved in a solvent of sufficient amount to saturate the support without leaving any free liquid, followed by impregnation of the support with the solution, and drying. Deionized water was used as the solvent in the preparation of the various catalysts. The wet point of the supports, the point at which the support is saturated with solvent, was determined by the slow addition of deionized water or metal salt solution to a measured quantity of support until free liquid appeared. The wet point of the supports varied depending on the metal salt and the concentration of solution used. For preparations of catalysts with loadings greater than four per cent by weight, the wet point was determined with a solution of the metal salt.

The supports used in catalyst preparation were activated alumina, 8-14 mesh (Matheson Coleman and Bell) and silica gel, 6-16 mesh, grade 05 (Matheson Coleman and Bell). The supports were dried at 120°C overnight prior to use.

A general procedure for preparation of the supported catalysts is as follows: the desired amount of metal salt was dissolved in a suitable quantity of water and was added slowly to the proper amount of support with rapid stirring. After addition of the solution, the catalyst was dried at 120°C overnight. Typical examples of the preparation of two silica supported catalysts are given below.

A copper catalyst supported on silica gel was prepared by the slow addition of a solution consisting of 3.5063 grams of
Cu(NO$_3$)$_2$·3H$_2$O (Fisher Scientific Company) and 0.0192 grams of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (Mallinckrodt Analytical Reagent) dissolved in 25.0 ml of water to 76.9 grams of silica with rapid stirring. The mixture was dried at 120°C overnight. This preparation gives an atomic ratio of Cu$_{133}$Mo$_1$ at a 1.21 weight per cent metal content.

A silica gel-supported cobalt molybdate catalyst was prepared by adding a solution consisting of 8.2341 grams of Co(NO$_3$)$_2$·6H$_2$O (Fisher Scientific Company) and 9.9825 grams of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O dissolving in 25.0 ml of water to 54.8 grams of silica with rapid stirring. The resulting mixture was dried at 120°C overnight yielding a catalyst with an atomic ratio of Co$_1$Mo$_2$ at a 12.9 per cent by weight metal content.

The unsupported cobalt molybdate catalyst was prepared in the following manner: a mixture of 29.5 grams of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and 33.3 ml of water was heated to 65°C and filtered. This solution was added to 24.5 grams of Co(NO$_3$)$_2$·6H$_2$O in 29.4 ml of water. The active component was precipitated by the addition of 26.7 ml of a 14.0 per cent by weight ammonium hydroxide solution at 50-60°C. The precipitate was filtered upon cooling, washed with water (100 ml), and dried at 120°C for four hours. The dried precipitate was broken up and sieved to approximately 10 mesh. The atomic ratio of the catalyst was Co$_1$Mo$_2$.

The procedure used in calcining the catalysts was as follows: the catalyst, approximately 4.70 cubic centimeters, was loaded into
the reactor and held in place by two stainless steel plugs (100 mesh). The reactor was connected to the apparatus and with an air flow of 550 ml per minute the reactor temperature was slowly raised to 500°C over a 90 minute period. This temperature was maintained for 120 minutes, followed by cooling in the presence of the air flush.

Oxidation Run Procedures

In the screening of catalysts, the effect of various reaction parameters upon the behavior of catalysts were evaluated by the pivot point technique. This involved the variation of certain reaction parameters with respect to a set of central reference conditions, termed the "pivot point". The pivot point was chosen as a temperature of 400°C, a contact time of 0.5 seconds, and a feed of 15 volume % hydrocarbon, 50% air, and 35% steam. These conditions were based upon literature data and the results of preliminary runs. The reaction parameters that were studied included the temperature, contact time, air to hydrocarbon ratio, volume per cent of water, and volume per cent of hydrocarbon in feed. Conditions employed in the screening of catalysts are given in Table VI.

To begin a run or a series of runs, the air flow was started and the components of the system were brought up to temperature. Stage one of the steam generator was operated at 110°C and stage two at 180°C. The preheater was maintained at 50°C less than the reactor temperature while the reactor exit line was kept at 300°C. The scrubber assembly was maintained at 45°C to prevent condensation
<table>
<thead>
<tr>
<th>Oxidation Run</th>
<th>Temp. (°C)</th>
<th>Contact Time (sec)</th>
<th>% Hydro-Carbon</th>
<th>% Air</th>
<th>% H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>400</td>
<td>0.5</td>
<td>15</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>B</td>
<td>475</td>
<td>0.5</td>
<td>15</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>C</td>
<td>500</td>
<td>0.5</td>
<td>15</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>D</td>
<td>400</td>
<td>0.25</td>
<td>15</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>E</td>
<td>400</td>
<td>1.0</td>
<td>15</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>F</td>
<td>400</td>
<td>0.5</td>
<td>15</td>
<td>75</td>
<td>10</td>
</tr>
<tr>
<td>G</td>
<td>400</td>
<td>0.5</td>
<td>5</td>
<td>17</td>
<td>78</td>
</tr>
</tbody>
</table>
of C_5 or lower hydrocarbons. When the components of the system reached the proper temperatures, water injection was begun and the scrubber was charged with 10 ml of water and 0.10 grams of hydroquinone inhibitor.

When the apparatus had stabilized at the desired temperatures, the syringe pumps were adjusted to give the desired flow rate of the piperylene mixture and water and the air flow adjusted to the proper flow rate for reaction conditions of the run.

The contact time was defined as the volume of unexpanded catalyst bed divided by the volume feed rate of reactant gas stream at reaction temperature and pressure (atmospheric). Ideal behavior of the gases was assumed.

After 50 minutes of equilibration, the scrubber was attached to the system and the timer started. As the run proceeded, 0.50 cc samples of the hydrocarbon stream were withdrawn from the sample port and analyzed on the gas chromatograph. These samples were generally taken at 15 minute intervals. After a number of samples were taken, usually five, the wet test meter was repositioned and carbon dioxide samples (0.50 cc) were taken at five minute intervals. Run times were generally limited to 40 to 90 minutes.

At the end of the run, the scrubber was disconnected and the timer stopped. The scrubber solution was worked up as previously described and stored at -15°C until analysis could be performed. The analysis was always performed within 24 hours.

After each run or every second run, depending upon the
severity of the oxidation, the catalyst was decarbonized at 500°C in the presence of air and steam.
RESULTS AND DISCUSSION

In the oxidation of piperylene, the method of vaporization of the piperylene feed material played an important role in the results observed. In preliminary runs, the piperylene mixture was vaporized by the infusion of the liquid feed to the "T" connector between the steam generator (stage two) and the preheater. This vaporization process, in which the liquid feed contacts the "T" connector at elevated temperatures, resulted in a polymer forming reaction occurring prior to the catalyst bed. Interestingly, no polymer formation was observed in the catalyst bed. Modification of the injector scheme (as described in the experimental section) so that vaporization occurred at ambient temperature, followed by dilution with air before preheating eliminated the polymer forming reaction.

While the manner of piperylene vaporization had little effect upon the type of products encountered over various catalysts, the yield of the products and the degree of conversion of the piperylene feed material were significantly affected. The conversions were lower in the oxidation runs with the modified injection scheme, while the product yields were substantially higher, indicating that polymerization was the major reaction occurring in the preliminary oxidation runs.

Over alumina supported catalysts, the oxidations were very exothermic. These oxidations were difficult to control and large amounts of cracking products were produced.
Carbonization of the catalysts also occurred, leading to a reduction in catalyst activity. Catalysts supported on silica gel were not as active as the alumina supported catalysts. Over these catalysts, the amount of cracking products was less than two per cent and these catalysts did not suffer from severe carbonization as did the alumina supported catalysts.

Oxidation over molybdenium promoted copper oxide and cobalt molybdate on silica catalysts, produced a large number of products. Typically, about 20 products were observed over copper oxide while approximately 30 products were found in the presence of cobalt molybdate. Of the 30 products found over cobalt molybdate, twenty were the same as those produced in the presence of copper oxide. Of these products, four have been identified: 2,4-pentadienal, 2,4-pentadienoic acid, acrylic acid, and 2-furaldehyde. Generally, the aldehydes were observed over both catalyst systems, with the dienal present in substantial quantities. While 2-furaldehyde was only present in trace quantities. The two carboxylic acids were formed only over the cobalt molybdate system and only in trace quantities. Treatment of the oxygenated product samples with 2,4-dinitrophenylhydrazine reagent leads to the classification of eight additional products. These eight products (peaks 3, 4, 8, 9, 14, 23, 24, and 26) were believed to be most probably aldehydes or ketones. There is the possibility that one or more of these products could be an allyl alcohol, since some allyl alcohols are known to be oxidized by the reagent to aldehydes or ketones, which then gives a
positive test.82

Table VII summarized the results obtained for runs with the molybdenum promoted copper oxide on silica gel catalyst. The yields of 2,4-pentadienal were based on the amount of cis- and trans-piperylene that was consumed during a run. Negative conversion values of particular components of the piperylene mixture was attributed to isomerization of one or more of the components in the piperylene mixture. In all conditions studied, 2-methyl-2-hexene was the most reactive of the components in the piperylene mixture. The relative reactivity of the other components, were dependent upon the reaction conditions of the runs.

No 2,4-pentadienoic acid was formed over this copper oxide catalyst at the conditions studied, while 2,4-pentadienal was observed in all except run C. The maximum yield of the aldehyde, 6.6%, occurred at the pivot point, run A. The effect of temperature upon the yield of the dienal was significant as shown in Figure 3. At 300°C (run C), no 2,4-pentadienal or any other product was observed. As the temperature was increased from 300° to 475°C (runs A, B, and C), the conversion of piperylene increased sharply while the yield of the aldehyde increased to a maximum at 400°C and decreased as the temperature was raised to 475°C. The influence of contact time upon the oxidation to 2,4-pentadienal is represented in Figure 4. The conversion of piperylene increased sharply as the contact time was increased, while the yield of the dienal reached a maximum at a contact time of 0.5 seconds then decreased as the contact time
## Table VII

Results for Molybdenium Promoted Copper Oxide Catalyst

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp. (°C)</th>
<th>Contact Time (sec)</th>
<th>% Diene</th>
<th>% Air</th>
<th>% Water</th>
<th>Conv. 2-methyl-2-butene</th>
<th>Conv. cyclo-pentene</th>
<th>Conv. trans-piperylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>400</td>
<td>0.5</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>37%</td>
<td>9.6%</td>
<td>11.5%</td>
</tr>
<tr>
<td>B</td>
<td>475</td>
<td>0.5</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>40%</td>
<td>14.7%</td>
<td>22.2%</td>
</tr>
<tr>
<td>C</td>
<td>500</td>
<td>0.5</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>18%</td>
<td>2.6%</td>
<td>-0.8%</td>
</tr>
<tr>
<td>D</td>
<td>400</td>
<td>0.25</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>37%</td>
<td>10.3%</td>
<td>4.6%</td>
</tr>
<tr>
<td>E</td>
<td>400</td>
<td>1.0</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>37%</td>
<td>16.6%</td>
<td>18.0%</td>
</tr>
<tr>
<td>F</td>
<td>400</td>
<td>0.5</td>
<td>15</td>
<td>75</td>
<td>10</td>
<td>29%</td>
<td>11.3%</td>
<td>7.7%</td>
</tr>
<tr>
<td>G</td>
<td>400</td>
<td>0.5</td>
<td>5</td>
<td>17</td>
<td>78</td>
<td>41%</td>
<td>22.6%</td>
<td>24.3%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Conv. cis-piperylene</th>
<th>Conv. total hydrocarbon</th>
<th>Conv. c- &amp; t-piperylene</th>
<th>Yield 2,4-pentadienal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-17.6%</td>
<td>8.0%</td>
<td>7.0%</td>
<td>6.6%</td>
</tr>
<tr>
<td>B</td>
<td>14.7%</td>
<td>20.4%</td>
<td>21.1%</td>
<td>4.7%</td>
</tr>
<tr>
<td>C</td>
<td>5.8%</td>
<td>0.9%</td>
<td>0.2%</td>
<td>0.0%</td>
</tr>
<tr>
<td>D</td>
<td>5.7%</td>
<td>6.5%</td>
<td>4.8%</td>
<td>1.1%</td>
</tr>
<tr>
<td>E</td>
<td>15.0%</td>
<td>17.7%</td>
<td>17.5%</td>
<td>5.9%</td>
</tr>
<tr>
<td>F</td>
<td>9.5%</td>
<td>8.9%</td>
<td>7.8%</td>
<td>0.9%</td>
</tr>
<tr>
<td>G</td>
<td>22.3%</td>
<td>24.1%</td>
<td>24.0%</td>
<td>5.4%</td>
</tr>
</tbody>
</table>
Figure 5. Effect of temperature upon conversion of piperylene and yield of 2,4-pentadienal over copper oxide.
Figure 4. Effect of contact time upon conversion of piperylene and yield of 2,4-pentadienal over copper oxide.
increased.

An increase in the oxygen to piperylene ratio and a decrease in the amount of steam (run F) resulted in a slight increase in conversion with a large decrease in the yield of the dienal. This observation is thought to be the result of a change in the active surface of the catalyst. The increase in the oxygen to piperylene ratio to an excess of one, leads to oxidation of the desired catalyst composition, cuprous oxide, to cupric oxide. Over cupric oxide, it is known that olefins are completely oxidized to carbon dioxide and water.

Interestingly, a significant increase in conversion and a slight decrease in yield of the aldehyde was observed in run G where the volume per cent of hydrocarbon was reduced and the amount of steam increased.

Table VIII summarized the results obtained for runs with the cobalt molybdate supported on silica gel catalyst. Similar to the copper oxide catalyst, 2-methyl-2-butene was more reactive than the other components of the piperylene mixture. In five of the runs, the relative order of reactivity of the remaining components of the piperylene mixture was:

trans-piperylene > cyclopentene > cis-piperylene

while in two runs, which had low conversions, the following order was observed:

cyclopentene > cis-piperylene > trans-piperylene.
### TABLE VIII

Results for Cobalt Molybdate Catalyst

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp. (°C)</th>
<th>Contact Time (sec)</th>
<th>% Diene</th>
<th>% Air</th>
<th>% Water</th>
<th>Conv. 2-methyl-2-butene</th>
<th>Conv. cyclopentene</th>
<th>Conv. trans-piperylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>400</td>
<td>0.5</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>36%</td>
<td>12.9%</td>
<td>14.3%</td>
</tr>
<tr>
<td>B</td>
<td>475</td>
<td>0.5</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>55%</td>
<td>21.4%</td>
<td>53.3%</td>
</tr>
<tr>
<td>C</td>
<td>300</td>
<td>0.5</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>46%</td>
<td>14.6%</td>
<td>-1.8%</td>
</tr>
<tr>
<td>D</td>
<td>400</td>
<td>0.25</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>41%</td>
<td>13.7%</td>
<td>1.9%</td>
</tr>
<tr>
<td>E</td>
<td>400</td>
<td>1.0</td>
<td>15</td>
<td>50</td>
<td>35</td>
<td>41%</td>
<td>16.3%</td>
<td>18.6%</td>
</tr>
<tr>
<td>F</td>
<td>400</td>
<td>0.5</td>
<td>15</td>
<td>75</td>
<td>10</td>
<td>19%</td>
<td>12.7%</td>
<td>16.0%</td>
</tr>
<tr>
<td>G</td>
<td>400</td>
<td>0.5</td>
<td>5</td>
<td>17</td>
<td>78</td>
<td>59%</td>
<td>20.9%</td>
<td>56.6%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Conv. cis-piperylene</th>
<th>Conv. total hydrocarbon</th>
<th>Conv. c-4t-piperylene</th>
<th>Yield 2,4-pentadienal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-1.1%</td>
<td>12.5%</td>
<td>12.0%</td>
<td>7.3%</td>
</tr>
<tr>
<td>B</td>
<td>-12.1%</td>
<td>40.0%</td>
<td>43.3%</td>
<td>6.2%</td>
</tr>
<tr>
<td>C</td>
<td>11.9%</td>
<td>3.5%</td>
<td>0.3%</td>
<td>0.0%</td>
</tr>
<tr>
<td>D</td>
<td>6.2%</td>
<td>5.1%</td>
<td>2.6%</td>
<td>11.0%</td>
</tr>
<tr>
<td>E</td>
<td>3.4%</td>
<td>16.7%</td>
<td>16.3%</td>
<td>11.0%</td>
</tr>
<tr>
<td>F</td>
<td>-6.1%</td>
<td>12.8%</td>
<td>12.6%</td>
<td>2.8%</td>
</tr>
<tr>
<td>G</td>
<td>5.2%</td>
<td>32.1%</td>
<td>31.8%</td>
<td>6.6%</td>
</tr>
</tbody>
</table>
A trace amount of 2,4-pentadienoic acid was observed over the cobalt molybdate catalyst in runs A, B, D, and G, while 2,4-pentadienal was observed in all except run C. The influence of temperature upon the degree of piperylene conversion and yield of the aldehyde (runs A, B, and C) is shown in Figure 5. The results were similar to those observed over the copper oxide catalyst, that is, the conversion increased sharply with temperature, while the yield of the dienal increased to a maximum at 400°C and then decreased as the temperature was increased to 475°C. The effect of contact time on conversion and yield of the aldehyde (runs A, D, and E) was significantly different than that observed over the copper oxide catalyst, as shown in Figure 6. As the contact time was increased from 0.25 to 1.0 seconds, the conversion increased less sharply, while the yield of the dienal was greatest at contact times of 0.25 and 1.0 seconds and decreased at a contact time of 0.5 seconds.

An increase in the oxygen to piperylene ratio and a decrease in the amount of steam (run F), resulted in little change in conversion of piperylene, while the yield of the aldehyde dropped substantially. A decrease in the amount of hydrocarbon in the feed and increase in the amount of steam resulted in a substantial increase in conversion with only a slight drop in yield of the aldehyde with both cobalt molybdate and copper oxide.

In run C, a number of products were formed that did not occur under any other reaction conditions or with any other catalyst studied. Besides the formation of eight new products, 12 compounds
Figure 5. Effect of temperature upon conversion of piperylene and yield of 2,4-pentadienal over cobalt molybdate.
Figure 6. Effect of contact time upon conversion of piperylene and yield of 2,4-pentadienal over cobalt molybdate.
including the dienal and 2,4-pentadienoic acid were absent in this run. This behavior is thought to be the result of a change in the mechanism of the oxidation. Over cobalt molybdate catalysts, the oxidation of certain olefins (propylene, the n-butenes, and the n-pentenes) at low temperatures (100-300°C) and in the presence of steam proceeds by a mechanism other than allylic oxidation. This mechanism involves the hydration of the olefin on an acidic site of the catalyst to form an alcohol intermediate, followed by oxydehydrogenation to yield a ketone.

\[
\begin{align*}
\text{CH}_2=\text{CH}-\text{R} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{CH}_3\text{-C}-\text{R} \quad \xrightarrow{\text{OH}} \quad \text{CH}_3\text{-C}-\text{R} + \text{H}_2\text{O} \\
\end{align*}
\]

As the temperature is increased above 300°C, the products became more typical of those of an allylic oxidation.

The unsupported cobalt molybdate catalyst produced the same types of products observed over the supported cobalt molybdate catalyst. The conversion was on the average, 30 per cent lower for the unsupported catalyst, while the yield of the dienal was higher by about 38%. Finally, over the cobalt molybdate catalysts, the yields of 2,4-pentadienal were consistently higher than that obtained in the presence of copper oxide, while the ratio of dienal to the total number of oxygenated products was less over copper oxide. This is attributed to the greater production of carbon dioxide over copper oxide.
CONCLUSIONS

Inspection of the results obtained in this project lead to the following conclusions:

1. The method of hydrocarbon feed vaporization plays an important role in the type of reaction that occurs. To avoid unwanted side reactions, the feed should be vaporized at low temperatures and diluted with air before preheating.

2. Alumina could not be used as a catalyst support, since severe cracking and carbonization occurred over this support. Silica gel did not crack piperylene severely and can be used for the supporting of catalysts.

3. Over copper oxide and cobalt molybdate, piperylene is converted to numerous products. A greater number of products was observed over cobalt molybdate.

4. The desired product, 2,4-pentadienoic acid, was observed only in the presence of cobalt molybdate and in trace amounts. 2,4-Pentadienal was observed over all catalysts.

5. The highest yield of 2,4-pentadienal, 11% was observed over cobalt molybdate.

6. It is suggested that the project be continued with the evaluation of other catalysts. Emphasis should be placed upon investigations involving the use of two catalysts for producing 2,4-pentadienoic acid. One catalyst for production of 2,4-pentadienal, followed by oxidation of
the dienal to the acid over a second catalyst.
REFERENCES


(68) Butt, N. S., and Fish, A. (1966), ibid., 508.


