The Liquid Phase Oxidation of 1,3-Pentadiene

1977

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THE LIQUID PHASE OXIDATION
OF 1,3-PENTADIENE

BY

CARL B. REAVES
B.A., University of South Florida, 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
1977
ABSTRACT

The liquid phase autoxidation of 1,3-pentadiene to 2,4-pentadienoic acid utilizing gaseous oxygen at atmospheric pressure was investigated as a possible route for direct utilization of piperylene obtained during the cracking of naptha to ethylene.

Catalyst systems consisting of cobalt, manganese, and iron salts promoted by sodium, potassium and hydrogen bromides, were used under a variety of conditions of catalyst concentration, temperature, oxygen flow and piperylene purity.

Under all conditions studied, a large number of oxidation products were formed. Maximum yields of 2,4-pentadienoic acid were obtained using a cobalt acetate bromide catalyst at 85°C.
ACKNOWLEDGEMENTS

The author would like to sincerely thank Dr. Guy C. Mattson, who directed this research project for his instruction, assistance, patience and personal motivation.

The author would also like to thank Dow Chemical U.S.A., Louisiana Division, for both financial support and the loan of equipment.

Finally, the author would like to thank his parents for their support during graduate and undergraduate years.
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INTRODUCTION

Classical Autoxidation

Historically, the oxidation of organic compounds has been studied for a considerable period of time\(^1\)-\(^2\). In 1774, Priestly's discovery of oxygen and Lavoisier's explanation of combustion initiated the start of the modern era of chemistry. The first studies performed in the nineteenth century associated the deterioration of many organic substances including rubber and natural oils, to the absorption of oxygen. These studies were primarily concentrated on inhibiting these processes. During the turn of the century, organic peroxide formation was determined to be involved in these processes. Studies based on the observations made with simple hydrocarbons and molecular oxygen interaction, performed in the 1940s, led to the development of the free radical chain theory of autoxidation. This was primarily due to Professor Gee and his colleagues, notably Farmer and Bolland, who were then working in the laboratories of the British Rubber Producers Association\(^3\),\(^4\). They recognized that removal of a hydrogen atom was the first step, and that a hydroperoxide was the primary product of the oxidation. They established by kinetic experiments the radical reaction sequence that led to hydroperoxide formation.

Homogeneous catalysis has received renewed interest during the last twenty years. This is partially attributed to the renaissance of inorganic chemistry in which emphasis has been placed on the preparation and properties of coordination complexes of transition metals.
Much emphasis has also been placed upon the understanding of the basic role of transition metal complexes in liquid phase autoxidations.

The liquid phase oxidation of hydrocarbons via molecular oxygen provides the basis for a number of commercial industrial chemical processes $^{5-17}$, such as the production of phenol and acetone from cumene, adipic acid from cyclohexane, terephthalic acid from p-xylene, acetaldehyde and vinyl acetate from ethylene and a number of others. These processes utilize catalysis by transition metal complexes for greatest selectivity and efficiency.

Many liquid phase oxidations, known as autoxidations occur spontaneously under relatively mild conditions of temperature and oxygen pressure. They are characterized by autocatalysis by the product, with the simpler oxidations giving rise to high yields of hydroperoxides, and the more complex oxidations giving rise to a wide range of products. With few exceptions, the majority of liquid phase autoxidations proceed by a free radical chain mechanism. The basic reaction scheme is that established by Bolland $^3$ who worked with olefinic esters that gave high yields of hydroperoxides.

This reaction scheme comprises three types of steps. These are (1) initiation, (2) propagation and (3) termination and may be represented by the following reaction sequence:

**Initiation:**

$$\text{RH} \xrightarrow{\text{activation}} \text{R}^\cdot + (\text{H}^\cdot)$$  \hspace{1cm} (1)

**Propagation:**

$$\text{R}^\cdot + \text{O}_2 \rightarrow \text{RO}_2^\cdot$$  \hspace{1cm} (2)
\[ \text{RO}_2^\cdot + \text{RH} \xrightarrow{K_p} \text{RO}_2\text{H} + \text{R}^\cdot \]  

(3)

Termination: \[ \text{R}^\cdot + \text{RO}_2^\cdot \rightarrow \text{RO}_2\text{R} \]  

(4)

\[ 2\text{RO}_2^\cdot \xrightarrow{2K_t} \text{RO}_4\text{R} \rightarrow \text{non-radical products} + \text{O}_2 \]  

(5)

Where \( \text{R}_i \) is the rate of chain initiation and \( K_p \) and \( K_t \) are respective propagation and termination rate constants. Alkylperoxy radicals play vital roles in both the propagation and the termination steps. Hydroperoxides, \( \text{RO}_2\text{H} \), are usually the primary products of liquid phase autoxidations and may be isolated in high yields in many cases. Much of the current knowledge concerning autoxidation mechanisms has resulted from the studies of the reactions of alkylperoxy radicals\(^{18-21}\) and the parent hydroperoxides\(^{22-25}\), independent of autoxidation.

At partial pressures of oxygen greater than 100 Torr, chain termination occurs exclusively via the destruction of two alkylperoxy radicals (reaction 5). The crosstermination reaction (4) may be neglected and the predicted rate expression, under steady-state conditions, is given by:

\[ \frac{-d[\text{RH}]}{dt} = \frac{-d[\text{O}_2]}{dt} = \text{R}_p[\text{RH}][\frac{\text{R}_i}{2K_t}]^{1/2} \]  

[1]

This expression accounts for the familiar S-shaped oxidation/time curves; the reaction accelerates as hydroperoxide is built up, and then slows down as the substrate is used up.

**Initiation**

Chain initiation is the primary production of free radicals
These radicals may arise by (a) heat, light or ionizing radiation, (b) by adding initiators which thermally decompose into radicals, (c) by thermal decomposition into radicals of the hydroperoxide produced in the reaction, (d) by the reaction of a metal catalyst with hydroperoxides to form radicals, (e) by direct reaction between oxygen and the substrate which is thought to be operative only at high temperatures and (f) by reaction of the substrate and a metal ion in a higher state of oxidation. Of these, the thermal decomposition of the alkyl hydroperoxide represents a major source of free radicals in autoxidation reactions.

If initiation involves simple unimolecular homolysis of the alkyl hydroperoxide, the initiating steps can be represented as:

\[
\text{ROOH} \xrightarrow{k_1} \text{RO}^+ + \cdot \text{OH} \quad (6)
\]

\[
\text{RO}^+ + \text{RH} \rightarrow \text{ROH} + \text{R}^+ \quad (7)
\]

\[
\cdot \text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^+ \quad (8)
\]

where \(k_1\) is the rate constant for hydroperoxide decomposition. It is observed that substantial amounts of RH are attacked by alkoxy and hydroxy radicals generated from the thermolysis of the hydroperoxide.

**Propagation**

Propagation is the repetition of a pair of reactions (2) and (3) which produce one molecule of hydroperoxide, and regenerate the \(\text{R}^+\) radical. The addition of the radical (\(\text{R}^+\)) to oxygen is extremely rapid for nearly all hydrocarbon radicals. Therefore, only alkylperoxy...
radicals are of importance in chain propagation and termination reactions except at a very low partial pressure of oxygen or with very reactive organic substrates\(^3,27\). At partial pressures above 100 Torr, the rate controlling step in autoxidations is hydrogen transfer from the substrate to the alkylperoxy radical, reaction (3). The rate constants for hydrogen transfer from a similar compound can be roughly correlated with the exothermicity of reaction (3).

In the absence of major steric effects, the rate of reaction (3) depends upon the carbon hydrogen bond strength, the resonance stabilization of the alkyl radical being formed\(^3,28\), and the availability of electrons at the carbon-hydrogen bond being broken\(^29-31\).

Alkylperoxy radicals, being relatively stable and unreactive, are quite selective and preferentially abstract the most weakly bound hydrogen. The selectivity of alkylperoxy radicals is similar to that of bromine. The relative rates of attack on the primary, secondary and tertiary C-H bonds of 2-methyl pentane are roughly in the order 1:30:300\(^32\).

Propagation rate constants have been found to depend not only upon the substrate but also upon the nature of the attacking alkylperoxy radical. These rate constants are measured experimentally by carrying out the autoxidations of various substrates RH in the presence of moderate concentrations of an alkyl hydroperoxide \(R'\text{O}_2\text{H}\). Under these conditions all of the alkylperoxy radicals derived from RH undergo chain transfer with the added hydroperoxide,

\[
\text{RO}_2' + \text{R'}\text{O}_2\text{H} \rightarrow \text{RO}_2\text{H} + \text{R}'\text{O}_2' \tag{9}
\]
and the rate controlling propagation and termination steps are represented by:

\[
R'\text{O}_2^- + RH \xrightarrow{k_p^-} R'\text{O}_2H + R^-
\]

\[
2R'\text{O}_2^- \xrightarrow{2k^-t} \text{non-radical products}
\]

The overall rate of oxidation is given by:

\[
-\frac{\alpha[O_2]}{\text{at}} = k_p^\prime[RH] \left(\frac{R_t}{2k^-t}\right)^{1/2}
\]

and determination of the absolute rate constants gives the "crossed" propagation rate constant, \(k_p^\prime\).

In Table I the rate constants, \(k_p^\prime\), for reaction of several substrates with tert-butylperoxy radicals are compared with the rate constants, \(k_p\), for reaction with their own peroxy radicals.

Table I also shows that the reactivities of peroxy radicals are strongly dependent on their structure. Reactivities are influenced by both steric and polar effects, and in general, increase as the electron withdrawing capacity of the \(\alpha\) substituent increase. Acylperoxy radicals, which possess a strong electron-withdrawing substituent, are considerably more reactive than other alkyperoxy radicals. This is seen in the case of the benzoylperoxy radical which is \(4 \times 10^4\) times more reactive than the tert-butylperoxy radical.

**Addition Mechanisms**

There are additional possibilities for chain propagation in the autoxidation of olefins. These reactions involve the addition of the
<table>
<thead>
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<th>Structure</th>
<th>$k_p(M^{-1}sec^{-1})$</th>
<th>$k_{p}^o(M^{-1}sec^{-1})$</th>
<th>$k_p/k_{p}^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>octene-1</td>
<td>$CH_2=CH(CH_2)_5CH_3$</td>
<td>0.5</td>
<td>0.084</td>
<td>6.0</td>
</tr>
<tr>
<td>cyclohexene</td>
<td></td>
<td>1.5</td>
<td>0.80</td>
<td>1.9</td>
</tr>
<tr>
<td>cyclopentene</td>
<td></td>
<td>1.7</td>
<td>0.85</td>
<td>2.0</td>
</tr>
<tr>
<td>2,3 Dimethylethyl butene-2</td>
<td>$CH_3-C-C=CH_2$</td>
<td>0.14</td>
<td>0.14</td>
<td>1.0</td>
</tr>
<tr>
<td>toluene</td>
<td>$CH_3-CH_3$</td>
<td>0.08</td>
<td>0.012</td>
<td>6.7</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>$CH_3-C_2H_5$</td>
<td>0.65</td>
<td>0.10</td>
<td>6.5</td>
</tr>
<tr>
<td>cumene</td>
<td>$CH_3-CH(CH_3)_2$</td>
<td>0.18</td>
<td>0.22</td>
<td>0.9</td>
</tr>
<tr>
<td>teratalin</td>
<td></td>
<td>1.6</td>
<td>0.5</td>
<td>3.2</td>
</tr>
<tr>
<td>benzyl ether</td>
<td>$CH_3-O-CH_3$</td>
<td>7.5</td>
<td>0.3</td>
<td>25.0</td>
</tr>
<tr>
<td>benzyl chloride</td>
<td>$CH_3-CH_2Cl$</td>
<td>1.50</td>
<td>0.008</td>
<td>190.0</td>
</tr>
<tr>
<td>benzyl bromide</td>
<td>$CH_3-CH_2Br$</td>
<td>0.6</td>
<td>0.006</td>
<td>100.0</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>$CH_3-CHO$</td>
<td>33,000</td>
<td>0.85</td>
<td>$\sim 40,000$</td>
</tr>
</tbody>
</table>
alkylperoxy radical to the double bond

$$\text{RO}_2 \cdot + \text{C} = \text{C} \rightarrow \text{RO}_2\text{C-C} \cdot$$

followed by reactions that lead to epoxide formation,

$$\text{RO}_2\text{C-C} \cdot + \text{C} = \text{C} \rightarrow \text{C-O-C} + \text{RO} \cdot$$
or polyperoxide formation

$$\text{RO}_2\text{C-C} \cdot + \text{O}_2 \rightarrow \text{RO}_2\text{C-CO}_2 \text{ etc.}$$

Much of the present knowledge of the addition mechanism of olefin autoxidation resulted from the studies of F. R. Mayo and his coworkers. They noted that the abstraction of hydrogen from the olefin by alkylperoxy radicals occurred exclusively at the reactive allylic position. Abstraction and addition are competing processes in olefin oxidations. The ratio of addition to abstraction products is strongly dependent on the structure of the olefin as mentioned earlier.

**Termination**

Under normal conditions of autoxidation, termination steps occur solely by the reaction of pairs of alkylperoxy radicals, which combine to form unstable tetroxides or polymeric peroxides:

$$2\text{RO}_2 \cdot \nrightarrow \text{RO}_4\text{R} \quad (11)$$
or

$$2\text{RO}_2 \cdot \nrightarrow \text{ROOR} + \text{O}_2 \quad (12)$$

The modes of decomposition of the tetroxides are dependent on
the structure of the alkyl group. 18-21,38,39

The termination product ROOR is a peroxide and can itself, act as an initiator.26 This is thought to be important at high temperatures. Because of this, and because of lower oxygen solubility and the fact that reaction (3) has a higher energy of activation than reaction (2), it is possible that at high temperatures, termination takes place mainly by reaction (4) with a consequent alteration in kinetics and products of the oxidation.

The overall rate of autoxidation of a substrate is determined then by both the propagation rate constant, Kp, and the termination rate constant, Kt, as given in Equation 1. Table II lists approximate rate constants for various peroxy radical terminations. It is seen in Table II that the lower rates of autoxidation for primary and secondary hydrocarbons when compared to tertiary hydrocarbons is not only due to the lower reactivity of the C-H bonds in the former but also significantly higher rates of termination of primary and secondary alkylperoxy radicals. Primary and secondary peroxy radicals can also terminate reaction chains by way of a cyclic transition state.

\[ \begin{align*}
2 \text{CH}_3\text{CHOO}^- &\rightarrow \text{CH}_3\text{C}_6\text{H}_5\text{O}^- + \text{CH}_3\text{C}_6\text{H}_5\text{O}^- \\
&\rightarrow \text{CH}_3\text{C}_6\text{H}_5\text{CHCH}_3^- + \text{H}_2\text{O} + \text{CO}_2
\end{align*} \quad (13) \]

Tertiary peroxy radicals terminate reaction chains less readily, since they lack a hydrogen atom on the α carbon. It is generally assumed that these radicals undergo a non-terminating interaction.
**TABLE II**

Approximate Rate Constants for Various Alkylperoxy Radical Terminations at 30°C

<table>
<thead>
<tr>
<th>Alkylperoxy Radical</th>
<th>$2Kt \ (M^{-1 \ sec^{-1}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO$_2^•$</td>
<td>$7.6 \times 10^5$</td>
</tr>
<tr>
<td>Primary RCH$_2$O$_2^•$</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Secondary R$_2$CHO$_2^•$</td>
<td>$10^6$</td>
</tr>
<tr>
<td>Tertiary R$_3$CO$_2^•$</td>
<td>$10^3$</td>
</tr>
</tbody>
</table>
to produce alkoxy radicals,

\[ 2R_3CO_2^- \rightarrow 2R_3CO + O_2 \]  

(14)

which may dimerize, possibly while still in the same "solvent cage", disproportionate with the transfer of an alkyl group, decompose, or abstract a hydrogen from the substrate.

Effect of Metal Ions

A. Mechanisms of Redox Catalysis by Transition Metal Complexes

Electron and Ligand Transfer Processes.

The mechanisms of electron transfer processes involving metal ions have been studied by Taube, Gould, Reynolds, Kochi, etc. in recent years. It is now generally agreed and recognized that oxidation-reduction reactions involving metal ions and their complexes are of two types: inner sphere (ligand transfer) and outer sphere (electron transfer) reactions. Prototypes of these two processes are shown by the following reactions.

Electron transfer (outer sphere):

\[ \text{Co(NH}_3\text{)}_6^{3+} + \text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + \text{Co(NH}_3\text{)}_6^{2+} \]  

(15)

\[ K = 10^{-4} \text{ liter mole}^{-1}\text{sec}^{-1} \]

Ligand transfer (inner sphere):

\[ \text{Co(NH}_3\text{)}_5\text{Cl}^{2+} + \text{Cr}^{2+} \rightarrow \text{CrCl}^{2+} + \text{Co(NH}_3\text{)}_5^{2+} \text{ etc.} \]  

(16)

\[ K = 6 \times 10^5 \text{ liters mole}^{-1}\text{sec}^{-1} \]

It is noted that during electron transfer reactions, the coordination spheres of metal ions remain intact. In contrast, ligand
transfer reactions proceed via a bridge activated complex in which two metal ions are connected by a common bridging ligand.

These concepts of electron and ligand transfer have been applied to the oxidation and reduction of organic substrates by metal complexes\textsuperscript{55-58}. Therefore, the interconversion of carbonium ion ($R^+$), free radical ($R^\cdot$), and carbonion ($R^-$), can result from one equivalent change as depicted below.

\[
\begin{align*}
R^+ & \xrightleftharpoons{+e} R^\cdot \xrightleftharpoons{-e} R^- \\
\end{align*}
\]

J. K. Kochi\textsuperscript{58,59} showed that redox reactions of organic substrates with metal species involving one equivalent changes in the oxidation state of the metal would generate free radical intermediates. He also determined in this work that whether the subsequent reaction between a free radical and a metal complex occurs via electron transfer or ligand transfer was largely dependent upon the nature of the ligand. A unified theory of the mechanisms of the oxidation of alkyl radicals by copper(II) complexes was proposed by Waters and Kochi\textsuperscript{57-58} which is based on the hard and soft acid-base (HSAB) classification established by Pearson and others\textsuperscript{60-61}. When the metal is bonded to hard ligands such as the acetate ion, the reaction preferentially occurs at the metal atom (i.e. electron transfer). When the metal is bonded to soft ligands, such as bromide or iodide ion, the reaction occurs primarily on the ligand, and an atom transfer (inner sphere) mechanism usually prevails.

With these concepts in mind and the roles played by metal ions
and their complexes in the catalysis of oxidation reactions via homolytic mechanisms, it is seen that the catalytic action of metal complexes may involve any of the various initiation, propagation, and termination steps outlined earlier.

The participation of a metal catalyst in autoxidations can therefore be divided into the following groups: (a) reaction with peroxides; (b) reaction with substrate; (c) reaction with oxygen; and (d) reaction with alkoxy and alkyl peroxy radicals. It has been observed that the latter (d) leads to inhibition rather than to catalysis.²⁷

**Reactions of Metal Complexes with Peroxides**

There are extensive literature references concerning metal-catalyzed decompositions of peroxides.⁶²-⁶³ For the purpose of this paper, concentration will primarily be placed upon reactions of metal complexes with the alkyl hydroperoxides.

**A. Alkyl Hydroperoxides**

The most commonly accepted pathway for catalysis of liquid phase autoxidation reactions involves the metal catalyzed decomposition of alkyl hydroperoxides. Denisov and Emanuel provided much information concerning the roles of metal complexes in oxidations based upon studies under nonautoxidizing conditions; that is, by examining the decomposition of alkyl hydroperoxides alone in an inert atmosphere and an inert solvent.⁶⁴ The rapid decomposition of alkyl hydroperoxides in hydrocarbon solutions in the presence of trace amounts of iron, manganese, cobalt and copper napthenates has also been observed.⁶⁴-⁶⁶
The two reactions of hydroperoxides,

\[ \text{RO}_2\text{H} + M^{(n-1)+} \rightarrow \text{RO}^\cdot + M^{n+} + \text{HO}^- \]  
(18)

\[ \text{RO}_2\text{H} + M^{n+} \rightarrow \text{RO}_2^\cdot + M^{(n-1)+} + \text{H}^+ \]  
(19)

suggests a catalytic reaction is feasible since there is a regenerative pathway for the metal complex to react again with an alkyl hydroperoxide. However it is suggested that if a particular metal ion is capable of effecting only one of these reactions, stoichiometric and not a catalytic decomposition of the alkyl hydroperoxide would be expected. Moreover, metal complexes are described to initiate radical-induced chain decomposition of the hydroperoxide. Therefore a metal ion could produce radicals via reactions (18) or (19) which then causes the radical chain decomposition to occur:

\[ 2\text{RO}_2^\cdot \rightarrow 2\text{RO}^\cdot + \text{O}_2 \]  
(20)

\[ \text{RO}^\cdot + \text{RO}_2\text{H} \rightarrow \text{RO}_2^\cdot + \text{ROH} \]  
(21)

In this reaction sequence the metal ion is acting as an initiator rather than a catalyst.

It is possible to divide the metals that react with the alkyl hydroperoxide into four groups: (i) metals that effect reaction (18), (ii) metals that participate in reaction (19), (iii) metals that are involved in both, and (iv) metals that effect heterolytic reactions of the hydroperoxides. Other routes that do not involve changes in the oxidation state of the catalyst are also possible for homolytic
decomposition of the alkyl hydroperoxide $^1$.

**Metals that Effect and Participate in Reaction**

When the metal has two oxidation states of comparable stability, reactions (18) and (19) occur concurrently. Cobalt and manganese compounds are among the most effective catalysts for autoxidation since they are able to induce the catalytic (as opposed to stoichiometric) decomposition of alkyl hydroperoxides:

**Aqueous solution:**

\[
\text{RO}_2\text{H} + \text{Co(II)} \rightarrow \text{RO}^\cdot + \text{Co(III)OH} \tag{22}
\]

\[
\text{RO}_2\text{H} + \text{Co(III)} \rightarrow \text{RO}_2^\cdot + \text{Co(II)} + \text{H}^+ \tag{23}
\]

**Nonpolar solvents:**

\[
\text{RO}_2\text{H} + \text{Co(II)} \rightarrow \text{RO}^\cdot + \text{Co(III)OH} \tag{24}
\]

or

\[
\text{RO}_2\text{Co(II)} \rightarrow \text{RO}^\cdot + \text{Co(III)O} \tag{25}
\]

\[
\text{RO}_2\text{Co(III)} \rightarrow \text{RO}_2^\cdot + \text{Co(II)} \tag{26}
\]

In aqueous solution outer-sphere electron transfer between metal ions and alkyl hydroperoxides (reactions 22 and 23) is expected to be favorable. In nonpolar solvents electron transfer is suggested to proceed via the formation of inner-sphere, covalently bonded complexes. The overall reaction constitutes a catalytic decomposition of the hydroperoxide into alkoxy and alkylperoxy radicals:

\[
2\text{RO}_2\text{H} \rightarrow \text{RO}_2^\cdot + \text{RO}^\cdot + \text{H}_2\text{O} \tag{27}
\]
Cobalt compounds are generally the more effective catalyst and have received the most attention\textsuperscript{22,67-68}. One important point that is kept in mind from these studies is that radical-induced chain decomposition via reactions (20) and (21), is always in competition with decomposition via the foregoing cycle.

Hiatt \textit{et al.}\textsuperscript{22}, studied the decomposition of solutions of tert-butyl hydroperoxide in chlorobenzene at 25°C in the presence of catalytic amounts of cobalt, iron, cerium, vanadium, and lead complexes. The time required for complete decomposition of the hydroperoxide varied from a few minutes for cobalt carboxylates to several days for lead naphthenate. The products consisted of approximately 86% tert-butyl alcohol, 12% di-tert-butyl peroxide, and 93% oxygen, and were independent of the catalyst. A radical induced chain decomposition of the usual type\textsuperscript{69}, initiated by a redox decomposition of the hydroperoxide, was postulated to explain these results. When reactions were carried out in alkane solvents (RH), shorter kinetic chain lengths and lower yields of oxygen and di-tert-butyl peroxide were observed due to competing hydrogen transfer of tert-butoxy radicals with the solvent.

Competition between metal ion-induced and radical-induced decompositions of alkyl hydroperoxides is affected by several factors. First, the competition is influenced by the relative concentrations of the metal complex and the hydroperoxide. At high concentrations of the hydroperoxide relative to the metal complex, alkoxy radicals will compete effectively with the metal complex for the hydroperoxide.
Competition is also influenced by the nature of the solvent as noted above. Contribution from the metal-induced reaction is expected to predominate at low hydroperoxide concentrations and in reactive solvents. The contribution from the metal-induced decomposition to the overall reaction is readily determined by carrying out the reaction in the presence of free radical inhibitors, such as phenols, that trap the alkoxy radicals and, hence prevent radical-induced decomposition. Kamiya et al. showed that the initial rate of the cobalt catalyzed decomposition of tetralin hydroperoxide, when corrected for the contribution from radical-induced decomposition by the addition of an inhibitor, was (within experimental error) equal to the limiting rate of cobalt-catalyzed autoxidation of tetralin under the same conditions. This result demonstrated that under the autoxidizing conditions, chain initiation occurs exclusively via cobalt-catalyzed decomposition of the hydroperoxide.

Shchennekova and co-workers studied the influence of solvent on the relative rates of cobalt-catalyzed decomposition of the hydroperoxide. In polar solvents, such as water, carboxylic acids, or mixtures of carboxylic acids and chlorobenzene, reaction (22) was found to be the slower, rate determining step and the cobalt catalyst was found to exist almost completely in the divalent state during the reaction. In nonpolar solvents, such as benzene or chlorobenzene, reaction (23) was found to be the slower step and the catalyst was present mainly in the trivalent state. The reasons for this dramatic solvent effect have not been discussed to any length. It has been
suggested by Dennisov\textsuperscript{64} that in aqueous solution, reaction (23) takes place only between ionic species (Co\textsuperscript{3+} and RO\textsuperscript{2-}) and is very rapid. In a hydrocarbon medium, in which alkyl hydroperoxide does not dissociate appreciably, this reaction is expected to be very slow. Reaction (22), on the other hand may proceed via an inner-sphere, covalently bonded complex and should be facilitated in nonpolar, poorly coordinating solvents in which complex formation is more favorable. Exchange of ligands in Co(II) complexes, which are generally substitution labile, is rapid compared to Co(III) complexes, which are inert to substitution. A further point that is considered is that reaction (26) is reversible, whereas (24) is irreversible. The equilibrium constant of reaction (26) then is probably markedly dependent on solvent.

Hiatt \textit{et al.}\textsuperscript{22} reported that commencement of the cobalt-catalyzed autoxidation of pure hydrocarbons i.e., in nonpolar solvents, is accompanied by oxidation of Co(II) to Co(III). The transformation is easily observed by the change in color from pale violet or pink [Co(II)] to intense green [Co(III)]. Similarly, manganese-catalyzed autoxidation was observed to start when Mn(II) was converted to Mn(III). The concentration of Co(III) was observed to reach a maximum during the course of autoxidation and then decreased. This maximum was found to coincide with the appearance of aldehydes in the reaction mixtures. The authors also showed by calculation\textsuperscript{22} that reduction of Co(III) by a secondary product accounted for the observed kinetics much better than reduction by hydroperoxide. Hence, the decrease in concentration of Co(III) after it had reached a maximum was attributed to reduction.
by aldehydes, which was more facile than reduction by alkyl hydroperoxide (reaction 23).

The Mn(II)/Mn(III) system has not been studied in as much detail as cobalt. However, the principles discussed above can also be applied to the manganese-catalyzed reactions:

\[
\text{Mn(II)} + \text{RO}_2\text{H} \rightarrow \text{Mn(III)OH} + \text{RO}^* \quad (28)
\]

\[
\text{Mn(III)} + \text{RO}_2\text{H} \rightarrow \text{Mn(II)} + \text{RO}_2^* + \text{H}^+ \quad (29)
\]

As mentioned above, autoxidation studies\(^{22}\) indicate that reaction (28) is much faster than reaction (29) in hydrocarbon media. The kinetics of the reaction between manganous stearate and n-decyl hydroperoxide have been studied, and both metal induced and radical induced decomposition of hydroperoxide were observed.

**Activation of Molecular Oxygen by Metal Complexes**

The most common pathway for catalysis of autoxidations by transition metal complexes involves the decomposition of alkyl hydroperoxides. Another possible route for chain initiation involves direct oxygen activation. In this process, the complexation of molecular oxygen by a transition metal lowers the energy of activation for direct reaction with the substrate. For example, oxygen coordinated to a metal might be expected to possess properties similar to alkylperoxy radicals and undergo hydrogen transfer with a hydrocarbon.

\[
\text{M-O-O}^* + \text{RH} \rightarrow \text{M-O-OH} + \text{R}^* \quad (30)
\]

Many authors\(^{71-75}\) have proposed reaction (30) or a variation of it,
in an attempt to explain kinetic data. For example, Uri\textsuperscript{74} proposed the following mechanism for the initiation of cobaltous stearate-catalyzed autoxidation of methyl linoleate in benzene

\[
\text{Co(II) + } O_2 \rightarrow \text{Co(II)O}_2 \ \ \ \ (31)
\]

\[
\text{Co(II)O}_2 + \text{Co(II)XH} \rightarrow \text{Co(II)} + \text{Co(III)X} + \text{HO}_2^- \ \ \ (32)
\]

A number of transition metals are known to form stable dioxygen complexes, and many of these reactions have been found to be reversible\textsuperscript{76}. In the case of cobalt, numerous complexes have been shown to combine with oxygen reversible\textsuperscript{77}. Since cobalt compounds are also the most common catalysts for autoxidations, cobalt-oxygen complexes have often been implicated in chain initiation of liquid phase autoxidations. However, there is no evidence for chain initiation of autoxidations via an oxygen activation mechanism. Kochi\textsuperscript{1} suggests that such proposals are based upon kinetic evidence alone, and that many authors fail to recognize that conventional procedures for purifying substrates do not remove the last traces of alkyl hydroperoxides from many hydrocarbons. He further suggests that it is usually these trace amounts of alkyl hydroperoxide that are responsible for chain initiation during catalytic reaction with metal complexes.

Further evidence against initiation by direct oxygen activation in the oxidation of olefins was observed by Sheldon with the following observations\textsuperscript{78}. First, no reaction was observed between olefins (eg. cyclohexene, 1-octene and styrene) and metal dioxygen complexes \( \text{IrO}_2\text{Cl(Co)(PPh}_3\text{)}_2 \), \( \text{NiO}_2\text{(tBuCn)}_2 \) or \( \text{RhO}_2\text{Cl(CNCH}_3\text{)(PPh}_3\text{)}_2 \) when they were
heated in an inert atmosphere (nitrogen). Secondly, no catalysis was observed with these metal complexes in the autoxidation of olefins such as styrene, that could not form hydroperoxides. It is therefore concluded that at this time there is no bonafide evidence for initiation of autoxidations by direct hydrogen transfer between metal-dioxygen complexes and hydrocarbon substrates.

Reactions of Metal Complexes Directly with Substrate and Autoxidation

The classical method for carrying out catalytic oxidations of hydrocarbons substrates has involved the use of hydrocarbon itself as solvent and trace amounts of hydrocarbon-soluble metal complexes, such as metal stearates, naphthenates, or acetylacetonates, as catalysts. These reactions are generally carried out at low conversions to avoid excessive by-product formation. Catalysis involves redox reactions of the metal catalyst with intermediate hydroperoxides.

In recent years increasing use has been made of an alternative procedure involving the oxidation of hydrocarbon substrates in polar solvents, usually acetic acid, in the presence of relatively large amounts of metal catalyst, usually the metal acetate. These reactions are characterized by high rates of oxidation, high conversions, and more complete oxidation of the substrate. For example, the classic autoxidation of cyclohexane is carried out to rather low conversions and affords mainly cyclohexylhydroperoxide, cyclohexanol, and cyclohexanone. Autoxidation of cyclohexane in acetic acid, in the presence of substantial amounts of cobalt acetate catalyst, results in 75% selective formation of adipic acid at an 80% conversions.
In addition to the usual reactions of the catalyst with the intermediate hydroperoxides, the second type of reaction involves direct reaction of the metal catalyst with the hydrocarbon substrate and/or with secondary autoxidation products. Two possible pathways are considered for the product-ion of radicals via direct interaction of metal oxidant with hydrocarbon substrates.

Electron transfer:

$$\text{RH} + \text{M(OAc)}_3 \not\rightarrow [\text{RH}]^+ \text{M(OAc)}_2 + \text{AcO}^- \quad (33)$$

$$[\text{RH}]^+ \not\rightarrow \text{R}^+ + \text{H}^+ \quad (34)$$

Electrophilic Substrate:

$$\text{RH} + \text{M(OAc)}_3 \not\rightarrow \text{RM(OAc)}_2 + \text{HOAc} \quad (35)$$

$$\text{RM(OAc)}_2 \rightarrow \text{R}^+ + \text{M(OAc)}_2 \quad (36)$$

The overall result is a one-electron reduction of the metal oxidant with an accompanying formation of the substrate radical (R⁺) and is the same in both processes. The ease of electron transfer by a particular oxidant is related to their ionization potentials as listed in Table III. The ease of electrophillic substitution of a substrate by a metal complex is expected to parallel that of electron transfer. A distinction between the two processes on structure reactivity relationships alone is difficult. A clear delineation between the two processes would be provided by the observation of the intermediate species, i.e. the radical cation [RM]⁺ or the organometal [RM(OAc)₂].
### TABLE III

Ionization Potentials of Organic Substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>I.P. (eV)</th>
<th>Substrate</th>
<th>I.P. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkanes:</strong></td>
<td></td>
<td><strong>Aromatics:</strong></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>12.8</td>
<td>Nitrobenzene</td>
<td>10.0</td>
</tr>
<tr>
<td>Ethane</td>
<td>11.5</td>
<td>Benzene</td>
<td>9.25</td>
</tr>
<tr>
<td>Propane</td>
<td>11.1</td>
<td>Fluorobenzene</td>
<td>9.2</td>
</tr>
<tr>
<td>n-Butane</td>
<td>10.7</td>
<td>Chlorobenzene</td>
<td>9.1</td>
</tr>
<tr>
<td>Isobutane</td>
<td>10.6</td>
<td>Bromobenzene</td>
<td>9.0</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>10.5</td>
<td>Toluene</td>
<td>8.8</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>10.4</td>
<td>Ethylbenzene</td>
<td>8.75</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>9.9</td>
<td>Cumene</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-xylene</td>
<td>8.55</td>
</tr>
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<td></td>
<td></td>
<td>Mesitylene</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Anisole</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aniline</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Naphthalene</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Biphenyl</td>
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</tr>
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<td></td>
<td></td>
<td>Anthracene</td>
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</tr>
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<td></td>
<td></td>
<td>Methylnaphtalene</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methylanisole</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thioanisole</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetophenone</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Benzyl Chloride</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pyridine</td>
<td>9.25</td>
</tr>
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<td></td>
<td></td>
<td>Methyl pyridine</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>tert-Butylbenzene</td>
<td>9.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bezaldehyde</td>
<td>9.5</td>
</tr>
</tbody>
</table>

These two processes are used to exemplify redox reactions between metal complexes and hydrocarbon substrates, or secondary autoxidation products.

**Alkenes**

Baun and Sharp\(^7^9\) studied the reaction between various olefins and Co(III) salts in aqueous acid. The rate-determining step was considered to be the formation of the radical cation by one-electron transfer. In aqueous medium, this radical cation

\[
RCH = CH_2 + \text{Co(III)} \rightarrow RCH-CH_2 + \text{Co(II)}
\]  

(37)

then reacts with water to yield a complex mixture of aldehydes, carboxylic acids, ketones, and dienes.

The powerful one-electron oxidant, cobalt(III) trifluoroacetate, readily oxidized ethylene at ambient temperatures to afford ethylene glycol ditartrifluoracetate\(^8^0\). The oxidizing properties of cobalt(III) trifluoroacetate in trifluoroacetic acid are suggested to be due to the formation via dissociation of cationic species, such as Co\(^{+}(O_2CCF_3)_2\), which are very strong oxidants (electrophiles). The following electron transfer mechanism is suggested for the oxidation of ethylene:

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 + \text{Co(O}_2\text{CCF}_3)_2^+ & \rightarrow \text{CH}_2-\text{CH}_2 + \text{Co(O}_2\text{CCF}_3)_2^- \\
\text{CH}_2-\text{CH}_2 + \text{CF}_3\text{CO}_2\text{H} & \rightarrow \text{CF}_3\text{CO}_2\text{CH}_2\text{CH}_2^+ + \text{H}^+ \\
\text{CF}_3\text{CO}_2\text{CH}_2\text{CH}_2^+ + \text{Co(O}_2\text{CCF}_3)_3 & \rightarrow [\text{CF}_3\text{CO}_2\text{CH}_2]_2 + \text{Co(OCCF}_3)_2
\end{align*}
\]  

(38a, 38b, 39)
The oxidation of cyclohexene under the same conditions afforded a variety of products including cyclohexenyl and cyclohexyl trifluoroacetates, 1,2-cyclohexanediol ditrifluoroacetates, and a number of unidentified components. The complex mixture of products is thought to be formed via rearrangement of various cationic intermediates subsequent to the initial electron transfer process. As a preparative method, the oxidation of alkenes under these conditions suffers from the competitive addition of trifluoroacetic acid to the olefin:

\[
\text{C=C} + \text{CF}_3\text{CO}_2\text{H} \rightarrow \text{HC-C-O}_2\text{CCF}_3
\] (40)

The oxidation of olefins by manganese(III) acetate in acetic acid resulted in the formation of lactones,

\[
\text{RCH=CHR + Mn(OAc)}_3 \rightarrow \text{HC-C=CH-OCH}_2
\] (41)

and is analogous to the formation of lactones during the lead tetraacetate oxidation of olefins. The proposed mechanism involved the addition of carboxymethyl radicals, formed by the addition of acetic acid by Mn(III), followed by oxidation of the resulting radical.

A further variable in the oxidation of olefins by Mn(III) is the presence of halide ions. The oxidation of cyclohexene by Mn(III) acetate in acetic acid at 70°C was found to be very slow, but addition of potassium bromide led to rapid reaction. Cyclohexenyl acetate was formed in 83% yield.

Oxidation of alkenes to glycol mono- and diacetates have also
been reported to proceed with oxygen in acetic acid and in the presence of catalytic amounts of cerium acetate\textsuperscript{85}. It is assumed that reoxidation of Ce(III) to Cerum(IV) is a vital step in the catalytic cycle after electron transfer (equation 38). Ketones, esters and aldehydes have been oxidized by Mn(III) and Ce(IV) acetates to give radicals that can add to olefins to form a variety of products. For example the oxidation of acetone with Mn(III) or Ce(IV) acetate in the presence of olefins led to the following proposed reactions:\textsuperscript{83}

\[
\begin{align*}
\text{CH}_3\text{CCH}_3 + \text{Mn(III)[Ce(IV)]} &\rightarrow \text{CH}_3\text{CCH}_2 \cdot + \text{Mn(II)[Ce(III)]} + \text{H}^+ \\
\text{CH}_3\text{CCH}_2 \cdot + \text{RCH}=\text{CH}_2 &\rightarrow \text{RCHCH}_2\text{CH}_2\text{CCH}_3 \\
\text{RCHCH}_2\text{CH}_2\text{CCH}_3 + \text{Mn(OAc)}_3 \text{ or Ce(OAc)}_4 &\rightarrow \text{RCH}==\text{CHCH}_2\text{CCH}_3 + \text{RCHCH}_2\text{CH}_2\text{CCH}_3 + \text{OAc}
\end{align*}
\]

Aromatic Hydrocarbons

The metal-catalyzed oxidation of alkylated aromatic hydrocarbons forms a basis for a number of important industrial processes such as the manufacture of terephthalic acid by the liquid phase oxidation of p-xylene\textsuperscript{86-87}. These oxidations are usually carried out in acetic acid in the presence of high concentrations of cobalt and/or manganese acetate catalyst together with various promoters, such as metal bromides, aldehydes, or ketones. These oxidations have been found to involve a direct reaction between the aromatic hydrocarbon and the metal oxidant.

Dewar and coworkers\textsuperscript{88} studied the stoichiometric oxidation of
a number of aromatic ethers, and amines in acetic acid. The inverse
dependence on the rate of Mn(II) concentration was interpreted as a
reversible electron transfer oxidation by Mn(III) to form the aromatic
radical cation followed by rate determining loss of a proton. The
resultant benzlic radical is oxidized further by Mn(III). The overall
stoichiometry for the oxidation of p-methoxytoluene is illustrated by
the following equation:

\[
\text{CH}_3\text{O} - \text{CH}_3 + 2\text{Mn(OAc)}_3 \rightarrow \text{CH}_3\text{O} - \text{CH}_2\text{OAc} + 2\text{Mn(OAc)}_2 + \text{HOAc}
\]  

(45)

The catalytic process may be represented as:

\[
\text{ArCH}_3 + \text{Mn(III)} \nrightarrow \begin{cases} 
\text{[ArCH}_3\text{]}^+ + \text{Mn(II)} \quad (46) \\
\text{[ArCH}_3\text{]}^+ \rightarrow_{\text{slow}} \begin{cases} 
\text{ArCH}_2^+ + \text{H}^+ \quad (47) \\
\text{ArCH}_2^+ + \text{Mn(III)} \rightarrow_{\text{fast}} \begin{cases} 
\text{ArCH}_3^+ + \text{Mn(II)} \quad (48) \\
\text{ArCH}_2^+ + \text{HOAc} \rightarrow \text{ArCH}_2\text{OAc} + \text{H}^+ \quad (49)
\end{cases}
\end{cases}
\]

In this scheme, the rate of oxidation is dependent upon the ionization
potential of the aromatic substrate, and in agreement with an electron
transfer mechanism.¹

In contrast to oxidation with Mn(III) acetate, the oxidation
of alkylbenzenes by a stronger oxidant, Co(III) acetate, appeared to
involve only electron transfer. Waters and coworkers ⁸⁹ studied the
oxidation of a series of alkylbenzenes by Co(III) perchlorate in
aqueous acetonitrils. They observed a correlation between the reac-
tivity of the arene and the ionization potentials of the hydrocarbon
which was compatible with the formation of radical cations in an
electron transfer process. Other authors observed that the
relative rates of oxidation of alkylbenzenes by Co(III) acetate in
acetic acid are the reverse of what would be expected for a classical
free radical mechanism. For example, toluene is oxidized approximately
ten times as fast as cumene. Similarly, in the stoichiometric
oxidation of p-cymene by Co(III) acetate in acetic acid, product
formation occurred virtually exclusively via reaction at the methyl
group to give p-isopropyl benzyl acetate and p-isopropylobenzaldehyde.

\[
\text{CH}_3 \quad \text{Co(OAc)}_3 \quad \text{CH}_2\text{OAc} \quad \text{CHO} \\
\text{HOAc, 65°C} \quad \text{(81%)} \quad \text{(15%)}
\]

By contrast, oxidation of p-cymene by Mn(III) acetate gave products
derived from reactions of intermediate p-cymyl and carboxy methyl
radicals, indicating that reaction did not proceed via electron trans-
fer. Similarly the cobalt acetate catalyzed autoxidation of p-cymene
afforded mainly p-isopropylbenzoic acid derived from the selective
oxidation of the methyl group. Manganese acetate involved a catalyzed
autoxidation which gave mainly p-toluic acid and its precursor, p-
methylacetophenone. p-ethyltoluene, sec-butyltoluene and 1,1-di(p-
taly1) ethane similarly afforded products mainly derived from oxidation
of the methyl groups.
These results can be reconciled by a mechanism involving reversible formation of a radical cation by electron transfer oxidation of the hydrocarbon by Co(III):  

\[ \text{ArCH}_3 + \text{Co(III)} \rightarrow [\text{ArCH}_3]^+ + \text{Co(II)} \]  (51)

In the next step benzyl radicals are formed from the radical cation by loss of a proton:

\[ [\text{ArCH}_3]^+ \rightarrow \text{ArCH}_2^+ + \text{H}^+ \]  (52)

Products are then derived from subsequent reactions of the benzyl radical with Co(III) acetate,

\[ \text{ArCH}_2^+ + \text{Co(III)} \rightarrow \text{ArCH}_2^+ + \text{Co(II)} \rightarrow \text{ArCH}_2\text{OAc} \]  (53)

or under autooxidizing conditions, with oxygen,

\[ \text{ArCH}_2^+ + \text{O}_2 \rightarrow \text{ArCH}_2\text{O}_2^+ \rightarrow \text{products} \]  (54)

The authors suggested that proton loss (reaction 52) was controlled by stereoelectronic considerations and not by the thermodynamic stability of the product. In the preferred conformation, the tertiary hydrogen on the isopropyl group of the p-cymene radical cation is located in the nodal plane of the benzene ring where its interaction with the \( \pi \) system in the transition state is minimized. The methyl group, on the other hand, rotates rather freely, and the loss of any one of the hydrogens is, therefore, not conformationally restricted.

The same electron transfer mechanism was proposed by Heiba
et al.\textsuperscript{93}.

Despite much evidence in support of an electron transfer mechanism for the oxidation of aromatic hydrocarbons by Co(III), there is still much disagreement about the detailed mechanism, especially with less reactive alkyl aromatics. Several detailed kinetic studies of these reactions have been carried out both in the absence\textsuperscript{94-95} and presence\textsuperscript{96-97} of oxygen. The kinetics of these reactions are complicated by the fact that cobaltic acetate in acetic acid exists as a dimeric $\mu$-hydroxo species, which if formulated as (AcO)$_2$Co(OH)$_2$Co(OAc)$_2$.\textsuperscript{98} Moreover the rate determining step in reactions (51)-(53) may vary for different hydrocarbons, depending upon the stability of the radical cation that is formed. Most authors consider only reaction (51) to be reversible. However, reactions (52) and (53) may also be reversible. If it is assumed that reaction (53) is rate determining, the rate of reaction in the absence of oxygen should be second order in Co(III) concentration and independent of Co(II) concentration. Such kinetics have been observed in practice\textsuperscript{90}.

Effect of Halide Ions

The rates of oxidation of aromatic hydrocarbons are enhanced, often dramatically by the presence of halide ions. Bromide ions have been found to have a pronounced synergistic effect on cobalt- and manganese-catalyzed autoxidations of alkyl aromatic hydrocarbons\textsuperscript{67,99-106}. The discovery of this effect provided an important breakthrough in the manufacture of terephthalic acid\textsuperscript{99}. The normal cobalt-catalyzed autoxidation of $p$-xylene gives $p$-toluic acid, and further oxidation
is very slow. In the presence of sodium bromide, further rapid oxidation takes place and terephthalic acid is formed in near quantitative yields.

The addition of an equimolar amount of hydrogen bromide to cobalt(II) acetate in acetic acid produces cobalt acetate bromide.

\[ \text{Co(OAc)}_2 + \text{HBr} \rightarrow \text{Co(OAc)Br} + \text{HOAc} \] (55)

Hay and Blanchard\textsuperscript{67} believe this to be the active catalyst in the oxidation of hydrocarbons. p-Xylene is readily oxidized to terephthalic acid at atmospheric pressure and at temperatures as low as 60°-100°C. Tetralin is oxidized rapidly at room temperature to α-tetralone. The active catalyst is also formed from cobalt(II) acetate and metal bromides via the equilibrium.

\[ \text{Co(OAc)}_2 + \text{NaBr} \rightleftharpoons \text{Co(OAc)Br} + \text{NaOAc} \] (56)

High concentrations of catalyst (approximately 0.1 M), were required for optimum reaction rates. Other metal ions, such as cerium and manganese, showed the same effect, but to a more limited extent. None of the other halogens investigated, approached bromide in activity.

Hydrogen bromide enhanced the rate of autoxidation of cumene\textsuperscript{67}. This rate enhancement is best explained on the basis of equations [57], [58] and [59] as postulated by Vaughan, Rust and coworkers\textsuperscript{107}.

\[ \text{ROO} \cdot + \text{HBr} \rightarrow \text{ROOH} + \text{Br} \cdot \] [57]

\[ \text{Br} \cdot + \text{RH} \rightarrow \text{HBr} + \text{R} \cdot \] [58]
Such a scheme by itself is thought to be insufficient to explain the accelerating effect of hydrogen bromide on cobalt-catalyzed autoxidations, where optimum rates were achieved only in the presence of both hydrogen bromide and cobalt. One of the functions of the Co(II) may be to maintain the concentration of hydrogen bromide at a sufficiently low level by reaction (55), in order to prevent the acid catalyzed rearrangement of aralkyl hydroperoxides to phenols. A second function of the cobalt may be to reconvert benzylic bromides, formed during reaction, to bromide ion in order to maintain the catalyst. Thus, addition of cobalt(II) acetate to a warm solution of benzyl bromide in acetic acid immediately generated an intense blue color of cobalt acetate bromide:

\[
\text{Co(OAc)}_2 + \text{PhCH}_2\text{Br} \rightarrow \text{Co(OAc)}\text{Br} + \text{PhCH}_2\text{OAc}
\]

The rate enhancing effect of bromide ion has been explained by a scheme involving the formation of bromine atoms via electron transfer oxidation of bromide ion by Co(III):

\[
\text{Co(III)} + \text{Br}^- \rightarrow \text{Co(II)} + \text{Br}.
\]

\[
\text{ArCH}_3 + \text{Br} \rightarrow \text{ArCH}_2\text{Br}
\]

\[
\text{ArCH}_2\text{Br} + \text{O}_2 \rightarrow \text{ArCH}_2\text{O}_2\text{Br}
\]

\[
\text{ArCH}_2\text{O}_2\text{Br} + \text{Co(II)} \rightarrow \text{ArCHO} + \text{Co(III)}\text{OH}
\]

\[
\text{HBr} \rightarrow \text{Co(III)Br}
\]
Reaction (61) occurs instantaneously on mixing Co(III) acetate with lithium bromide in acetic acid\(^6^7\). A trace of tert-butyl hydroperoxide is required to initiate these reactions. Oxidation of Co(II) by hydroperoxide provided the Co(III) necessary for reaction (61).

In the presence of bromide ion there is no direct apparent reaction of Co(III) with the hydrocarbon substrate in contrast to cobalt-catalyzed autoxidations carried out in the absence of bromide. The fact that different mechanisms are operating is illustrated by the relative rates of oxidation of alkylbenzenes catalyzed by cobalt acetate compared to rates obtained in the presence of added bromide ion (Table IV). In the presence of bromide ion, the relative reactivities are consistent with a mechanism involving attack by bromine atoms but not one involving electron transfer. However, since the differences in selectivity between the two series are not large, it is suggested that the discrepancy can probably be attributed to the behavior of bromine atoms to the different conditions (solvent, temperature) under which the selectivities were measured. The rates of Co(III) oxidations have also been reported to be enhanced by chloride ions\(^9^3\). The oxidation of toluene by Co(III) acetate in acetic acid was found to require more than a week for the reaction at 65°C, but reacted in less than two hours at room temperature in the presence of a tenfold excess of lithium chloride. The products and relative reactivities of various alkylbenzenes were consistent with an electron transfer mechanism. This dramatic rate enhancement was attributed to the formation of a Co(III) complex of a higher oxidation potential\(^9^3\).
### TABLE IV

Relative Reactivities of Hydrocarbons Toward Cobalt Oxidation

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Relative reactivity (per active hydrogen)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Co(OAc)$_3$ (65°C)</td>
</tr>
<tr>
<td>Toluene</td>
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<tr>
<td>Ethylbenzene</td>
<td>1.3</td>
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<tr>
<td>Cumene</td>
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<td>p-Methoxytoluene</td>
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<tr>
<td>p-Xylene</td>
<td>10.3</td>
</tr>
<tr>
<td>Reference</td>
<td>124</td>
</tr>
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</table>
Holtz compared the oxidation of alkylaromatics with two different catalyst systems, $\text{Co(OAc)}_2\cdot\text{HCl}$ and $\text{Co(OAc)}_2\cdot\text{NaBr}$. Oxidations were carried out at high temperatures ($182^\circ\text{C}$) which are comparable to conditions of commercial processes. Oxidation of p-tert-butyltoluene and 2,2-bis(p-tolyl) propane in acetic acid, in the presence of $\text{Co(OAc)}_2\cdot\text{NaBr}$ gave the corresponding carboxylic acids in high yields.

By contrast, oxidations catalyzed by $\text{Co(OAc)}_2\cdot\text{HCl}$ were much less selective, and tert-butyltoluene gave considerable amounts of products resulting from C-C bond cleavage:
These results were explained by a radical mechanism involving bromine and chlorine atoms as the chain transfer agents, respectively, since it is known that chlorine atoms are much less selective than bromine atoms. Chlorine atoms were found to attack tert-butyl toluene at the methyl groups in the benzylic and β positions (i.e. tert-butyl). Bromine atoms on the other hand react selectively at only the benzylic methyl group. In general, the oxidation of aromatic hydrocarbons, carried out with high concentrations of cobalt catalyst involve the two competing processes of electron transfer oxidation of the hydrocarbon to the radical cation and electron transfer oxidation of the ligand to the corresponding radical:

\[
\text{Co(III)X} \xrightarrow{\text{ArH}} \text{Co(II) + [ArH]}^+ + \text{X}^- \quad \text{Co(II) + X}^-
\]
The relative rates of these processes are dependent on several factors: (1) the ionization potential of the hydrocarbon, (2) the oxidation potential of the anion in which the relative ease of oxidation is in the order \( \text{Br}^- > \text{Cl}^- > > \text{AcO}^- \) and (3) the temperature.

**Decomposition of the Hydroperoxide and Formation of Secondary Reaction Products**

The nature of the products and the mechanism by which they arise in the liquid phase oxidation of hydrocarbons has long been a subject of controversy. Invariably, a number of reaction products are formed by decomposition of the hydroperoxide. The oxidation of \( \text{n-heptane} \) gave a mixture of isomeric heptanones \( 108-109 \); the oxidation of octane, nonane, and decane gave a mixture of octanones, nonanones, and decanones \( 110 \), respectively, and the oxidation of cyclohexane gave cyclohexanol and cyclohexanone.

The initial point of oxygen attack in the hydrocarbon chain was the major subject under question. This problem has been largely resolved by recent work. Pope, Dystra and Edgar\(^{111}\) suggested that oxidation occurred first at the end of the chains (i.e. at a methyl group) of \( \text{n-octane} \) and branched chained octanes studied; it was considered that an aldehyde was formed, possibly via a peroxide, which then underwent stepwise oxidative degradation to aldehydes of shorter chain lengths by loss of water and carbon dioxide or carbon monoxide. On the other hand Ivanov, et al.\(^{112}\), studied the products from autoxidized n-heptane and stated that attack took place preferentially at the 2-position.
In another mechanistic scheme for the oxidation of long chain n-alkanes put forward by Leibnitz et al.\textsuperscript{113}, it was proposed that the initial reaction led to either a 1-hydroperoxide, and then a alkanal and 1-alkanoic acid or to a 3-hydroperoxide and then to an alkan-3-one; less attack occurred at C\textsubscript{4} and C\textsubscript{5} and even less beyond these positions and none at C\textsubscript{2}. These workers claimed that their evidence was not in agreement with statistical distribution of oxygen attack and random chain fission. When hydrocarbons containing tertiary C-H bonds were oxidized, alcohols and hydroxy groups on the tertiary C atoms (for example, 2,5-dimethyl hexan-2ol from 2,5-dimethylhexane\textsuperscript{114}) accumulated, together with carbonyl compounds formed by splitting of one end of the alkyl or aryl radicals from the tertiary carbon atom. The products of the oxidation of 2-methylheptane and 2,5-dimethylhexane contained acetone while those of the oxidation of 3-methylheptane contained methyl ethyl ketone, and those of the oxidation of triphenyl-methane contained benzophone\textsuperscript{115}.

It is now generally agreed that the composition of the products from the decomposition of the hydroperoxide is determined by the ratio between the energies of the rupture of the various bonds in the hydroperoxide molecule with respect to its structure\textsuperscript{66}.

The thermal decomposition of a primary hydroperoxide R-CH\textsubscript{2}OOH gave rise to the corresponding acid RCOOH, hydrogen H\textsubscript{2} and an ester \(\text{RC-O-CH}_2\text{R}\). An aldehyde is formed as a labile intermediate.

In order to provide an explanation for these types of autoxidation products, the following steps were proposed by Pritzkow\textsuperscript{109}:
The primary hydroperoxide adds to the aldehyde (formed via the above route) with the formation of a hydroperoxide which decomposes into an acid, an aldehyde, and H$_2$. The H$_2$ was reported to form from a CH$_2$ group as shown by an experiment on the decomposition of deuterated hydroperoxide RCH$_2$OOD$^{66}$. In this case only H$_2$ was formed, and no HD or D$_2$. The following decomposition mechanism was assumed:

$$\text{RCH}_2\text{OOH} + \text{RCHO} \rightarrow \text{RCH}_2\text{OOCR}$$

$$\text{RCH} \overset{\text{O-O}}{\rightarrow} \text{C-R} \rightarrow \left[ \begin{array}{c} \text{R-CH} \overset{\text{O}}{\rightarrow} \text{H} \overset{\text{H}}{\rightarrow} \overset{\text{OH}}{\text{C-R}} \end{array} \right] \rightarrow$$

$$\text{RCHO} + \text{RCOOH} + \text{H}_2.$$
The decomposition of secondary hydroperoxides is observed to give rise mainly to alcohols and ketones with the same number of carbon atoms as the initial hydroperoxide. The decomposition of tetra-alkyl hydroperoxide gave rise to the corresponding alcohol and ketone (a tetralone)\textsuperscript{116}. This ketone formation in the decomposition of secondary hydroperoxides takes place by the interaction of the hydroperoxide with free radicals:

\[
R_1\text{CHR}_2 + \text{RO}_2\cdot (R\cdot) + \text{ROOH} (R\cdot H); \\
\text{ROH} + \text{ROOH}
\]

\[
R_1\text{CR}_2 + \text{ROOH} (R\cdot H); \\
\text{ROH} + \text{ROOH}
\]

The C-H bond adjacent to the peroxy group is weakened and the radicals abstract an H atom predominately from this group.

The alcohol has been observed to form by two reactions: from the alkoxy radical (RO-) produced in the chain-branching reaction:

\[
\text{ROOH} \rightarrow \text{RO}^- + \cdot \text{OH} \\
\text{RO}^- + \text{RH} \rightarrow \text{ROH} + \text{R}^-
\]

and by a chain mechanism involving the interaction of the hydroperoxide with the radicals R\cdot and the RO\cdot radical\textsuperscript{66}.

The decomposition of tertiary hydroperoxides are suggested to take place by two routes. In the case of the primary and secondary hydroperoxides, the decomposition of tertiary hydroperoxides may yield the corresponding tertiary alcohols. In addition, the decomposition
of a molecule of tertiary hydroperoxide may be accompanied by the rupture of the carbon skeleton's tertiary carbon and possibly lead to formation of a ketone. Thus, for example, the decomposition of t-butyl hydroperoxide led to the formation of tertiary butyl alcohol and acetone:

\[
\text{CH}_3\text{C-C-OOH} \rightarrow (\text{CH}_3)_3\text{CO} + (\text{CH}_3)_2\text{CO} + \text{CH}_3
\]

The formation of alcohols in the decomposition of hydroperoxides is accompanied by the liberation of oxygen or the parallel oxidation of other components of the reaction mixture.

Subsequent Reactions of Dialkyl Peroxy Radicals

The products obtained when liquid olefin reacts with oxygen are divided into two categories: (1) the primary products produced in free radical propagation steps which require the consumption of oxygen and (2) the secondary products which are produced by subsequent ionic and radical reactions of the initial products. Hydroperoxides fit these criteria and more recently epoxides have been found to fit equally well. A third product whose occurrence is only suspected for nonconjugated olefins is the polyperoxides.

The contention that hydroperoxides, epoxides, and possibly polyperoxides are primary reaction products is discussed in terms of the following mechanism:
After initiating radicals are formed by hydroperoxide decomposition, the peroxy radical may react with the olefin by either alpha hydrogen abstraction (a), or by addition to the double bond (B). Abstraction results in the formation of an allylic radical which can react with oxygen to regenerate the same peroxo radical (or its allylic or cis-trans isomer). The net result of this propagating sequence is to yield hydroperoxide, the primary product from saturated hydrocarbons and nearly the exclusive product from olefins such as cyclohexene. These hydroperoxides in which the hydroperoxy group is present in the α position to double bond may also decompose by several routes which are:

1. by reaction with the initial hydrocarbon with the formation of an unsaturated alcohol with the same structure as the hydroperoxide

\[
\text{R-CH=CH}_2 + \text{RCH}_2\text{-CH}=\text{CH}_2 \rightarrow \text{RCH}=\text{CH}_2
\]

2. unimolecularly with the formation of an unsaturated alcohol and
oxygen, with the oxygen adding at the position of the double bond in the molecule of the alcohol to form an epoxy alcohol

\[
\text{RCH-CH=CH}_2 + \text{OOH} \rightarrow \text{RCHOH-CH-CH}_2
\]

and (3) unimolecularly with the formation of a vinyl ketone

\[
\text{R-CH=CH}_2 + \text{H}_2\text{O} \rightarrow \text{R} - \text{CH=CH}_2 + \text{HOOH}
\]

When the double bond is sufficiently reactive relative to the \(\alpha\)-hydrogen, addition (B) as well as abstraction (a) takes place. The peroxy radical intermediate which is formed is capable of either forming epoxide directly (c) or reacting further with oxygen as shown in (d). Subsequent reactions of the vinyl radical produced was found to lead eventually to the production of additional epoxide and a ketone or an aldehyde with one less carbon than the original olefin.

The mechanism involved in cleavage products resulting from possible decomposition of polyperoxide is still not entirely clear. However, decomposition of polyperoxides are expected to give predictable products.

Finally, in addition to the formation of products derived from the above routes, other secondary reactions may take place during olefin autoxidation\(^{118}\); these include (a) oxidation of the aldehydes present to acids, with the latter always being found in the products; (b) further oxidation of ketones (to diketones and then chain scission)
or unsaturated alcohols; (c) production of esters from alcohols, expoxides, glycols, acids, and aldehydes; (d) reaction of hydroperoxides with unsaturated ketones to yield expoxy ketones or peroxy ketones; (e) reaction of hydroperoxides with epoxides to give peroxides, which undergo further reaction; (f) rearrangement of epoxides and glycols to carbonyl compounds or unsaturated alcohols; and (g) formation of polymeric compounds.

In consideration of the various mechanisms involved in the autoxidation of olefins, an empirical rule established by Bolland for determining reactivity of olefins has been derived. This rule was derived from experimental data on the velocity constants of chain propagation reactions in the oxidation of olefins. All hydrocarbons investigated were considered as substituted proplyenes

\[ \text{CH}_3-\text{CH}═\text{CH}_2 \]

and it was shown that the rate of chain propagation reaction varied in accordance with the following laws:

1. the replacement of one or two hydrogen atoms in positions 1 and 3 by a methyl group or another alkyl group increases \( k_2 \cdot 3^n \) times, where \( n \) is the total number of alkyl groups introduced into positions 1 and 3; a similar replacement in position 2 has no effect whatever on the magnitude of \( k_2 \);

2. the replacement of an H atom in position 1 by a phenyl group increases \( k_2 \) by a factor of 23;

3. the replacement of an H atom in position 1 by an R-CH=CH group
increases $k_2$ by a factor of 107, and

(4) the inclusion of the group undergoing autoxidation in a cyclic structure additionally increases $k_2$ by a factor of 1.7.

Therefore, the substances formed by the decomposition of the hydroperoxides are intermediates in the reaction and during the further advance of the oxidative process they are converted completely to end products which are stable under the conditions of autoxidation.

**Purpose - Piperylene Oxidation**

Dow Chemical U.S.A., which funded this project has an interest in upgrading the value of some of the by-products obtained during the cracking of naptha to ethylene. Along the lines of the discussion in the previous section of this paper, attention was focused upon 1,3-pentadiene and the liquid phase oxidation products of this compound.

\[
\begin{align*}
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3 & \xrightarrow{[0]} \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2\text{OH} \\
\text{CH}_2=\text{CH}-\text{CH}=\text{CHO} & \\
\text{CH}_2=\text{CH}-\text{CH}=\text{OOOH} & 
\end{align*}
\]

These products could be used in synthesizing derivatives with potential usefulness.

It was decided to attempt the liquid phase oxidation of piperylene to the dienoic acid, utilizing gaseous oxygen at atmospheric pressure and a halogen promoted metal acetate catalyst system. These are the reaction conditions frequently employed in the oxidation of alkyl benzenes. It must be noted that the piperylene system
investigated here is a more complex system than the alkene and alkylated aromatic hydrocarbons discussed in previous sections. This is due to alternate reaction pathways (Fig. 1) of the initially formed peroxy radical. These alternate pathways are hydrogen abstraction and addition. Further oxidation and fragmentation of the products of these reactions could then lead to a variety of final products. Prior liquid phase work reported in the literature has involved simpler systems which could be anticipated to exhibit greater selectivity.
Figure 1. Possible Reaction Pathways
A diagram of the oxidation apparatus is given in Figure 2. The oxygen supply consisted of a section of $\frac{1}{4}$ inch diameter copper tubing fitted with a needle valve. The cylinder pressure reduced to 2-5 PSIG by a regulator supplied by Victor Equipment Company. A four inch length of the copper tubing extended from the needle valve to connect to an 18 inch length of $\frac{1}{2}$ inch diameter Tygon tubing which led to the first rotameter. A similar line for nitrogen purge was used and was also connected to this rotameter prior to oxidation run procedure. Through this tubing, a flow of oxygen, measured and controlled by a Linde Specialty Company rotameter entered the reaction flask via a fritted glass gas inlet tube.

The reaction flask was a 500 milliliter capacity, three neck flask with a thermowell and four indented sides similar to an Ace type 6958 Morton flask. The gas inlet tube, $\frac{24}{40}$, had a fritted glass porous tip of porosity designation Ace "A", Kimble 170-220. The flask was fabricated so the thermowell and gas inlet tube would provide maximum clearance for a paddle type stirrer. Temperature was monitored with a Precision Scientific mercury thermometer fitted into the thermowell. An explosion proof air stirrer by the Arrow Engineering Company was fitted to the reaction flask via a $\frac{45}{50}$ pyrex fitting. To the third neck of the reaction flask was fitted a $\frac{24}{40}$ ground glass "Ace" Claisen joint. The Claisen joint was fitted with a rubber septum which served as a sample port; and an Ace Glass Company Dry Ice
Figure 2. Oxidation Apparatus
condenser. This condenser was used to keep the low boiling hydrocarbon into the reaction flask.

A 20-inch length of $\frac{1}{4}$ inch diameter Tygon tubing extended from the dry ice condenser vent to a cold trap (Ace Glass Company) and a dewar flask for possible entrapment of any piperylene escaping from the reaction mixture as well as allow for $O_2$ flow throughout the system.

A second rotameter (Gilmont Company) measured the exit flow of oxygen and provided a means for monitoring the course of the reaction. To this rotameter was connected a final ten inch section of $\frac{1}{4}$ inch tygon tubing for outlet or venting purposes. This outlet tube was vented to the fume hood or connected to a wet-test meter, then vented. The reactor was sealed with vacuum grease and the stirrer lubricated with a silicone lubricant.

Power was supplied to the heating mantle by a variable transformer.

**Analytical**

Analysis of the samples of the reaction mixture was performed by a Hewlett-Packard model 5830A gas chromatograph equipped with a flame ionization detector and a 5830A programmable self-integrating chart recorder.

The column utilized in the gas chromatograph was a six-foot length of 1/8 inch outside diameter stainless steel tubing packed with 10% SP-1200 and 1% $H_3PO_4$ on acid-washed Chromosorb W, 80/100 mesh (Supelco, Incorporated). The column was initially conditioned at 190°C for two days at a helium carrier flow rate of 30 ml per minute.
The syringe used for reaction mixture sampling was a Glenco 10 ml glass syringe with a Leur Lock fitting graduated to 2/10 ml. The syringe used for sample introduction into the gas chromatograph was a Glenco 10 μl glass-metal syringe graduated in 1/10 μl. This syringe was rinsed with acetone and cleaned with a Precision Scientific syringe cleaner after sample introduction to keep down syringe clogging due to polymerization.

Analysis of the reaction mixture sample was carried out using a temperature program which initially held the G.C. column at 75°C for a period of five minutes, then caused the temperature to increase at a rate of 8°C per minute to 190°C, this temperature being maintained until all peaks had eluded. The chart speed was initially programmed at a rate of 2.5 cm per minute for three minutes then decreased to 1.0 cm per minute until all peaks had eluded also.

Typically, the reaction mixture samples produced the large series of peaks given in Table V. Comparison of the retention times for various standards with this data as well as Gas Chromatography-Mass Spec (Perkin Elmer-Bell and Howell) and the use of an internal standard gave the peak identities given in Table VI.

The internal standard for the programmable gas chromatograph which self-converted peak areas to weight percents which allowed for calculation to molar quantities was prepared as follows: a glass sample vial was weighed utilizing a Mettler balance and its weight was recorded. To this weighed sample vial was added 10.0354 g of reagent grade glacial acetic acid (Allied Chemical Company) solvent and its
TABLE V

Peak Retention Times for Reaction Mixture Effluent

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Retention Time (min)</th>
<th>Peak Size</th>
</tr>
</thead>
<tbody>
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<td>.57</td>
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<tr>
<td>2</td>
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<td>3</td>
<td>1,3-Pentadiene</td>
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<tr>
<td>4</td>
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<td>( \text{C}_5\text{H}_6\text{O} )</td>
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<tr>
<td>25</td>
<td>Trichlorobenzene</td>
<td></td>
</tr>
</tbody>
</table>
weight was recorded. 1,3-Pentadiene, 0.3451 g (.005 moles) (Chemical Samples Incorporated) was then added to the sample vial and its weight was recorded. This was designated as reference peak number two. 2,4-Pentadienoic acid, 0.4923 g (.005 moles) which was prepared in the laboratory was then added to the sample vial and its weight was recorded. This peak was designated as reference peak number 3 and the acetic acid component was designated as reference peak number 4. Each component's weight was then summed and subtracted from the sample vial weight. The resultant weight termed total sample weight was then recorded.

Trichlorobenzene, chosen as the internal standard was then added to the standard mixture and its weight was recorded separately. This was designated as reference peak number 1. This amount, 0.0178 g, corresponded to 0.103 weight percent of the internal standard mixture.

Trichlorobenzene was chosen as an internal standard because of its retention time and inertness in contrast to cyclohexanone which was initially utilized. The total sample weight was then divided into 100 to determine its XF value or its weight factor.

A 0.5 µl sample of this internal standard mixture was then introduced into the gas chromatogram and each respective component retention time was observed.

The retention time for each component was then programmed into the G.C. along with each component's respective weight in grams. The XF factor was then entered into the G.C. along with the corresponding internal standard amount. The standard sample was then injected (.5 µl) into the G.C. for expression of amounts of terms of weight percents
which could then be converted to molar quantity. This calculation was performed in terms of the amount trichlorobenzene internal standard present in the standard.

The analysis for 1,3-pentadiene, acetic acid, and 2,4-penta-dienoic acid was confirmed by manual calculation of weight percents in comparison to the g.c. calculations within the range of standard concentrations employed. These were respectively 3.169, 92.147 and 4.521 weight percents. This procedure was utilized for all samples taken during a typical run.

Analysis for determination of hydroperoxides and polymeric (alkyl) peroxides was also investigated. This employed iodine liberation Method I and Method III as reported by Mair and Graupner. Data obtained from these analysis are plotted in Figure 3. Hydroperoxide concentration determined here, demonstrated that as the 2,4-dienoic acid yield increases the hydroperoxide concentration decreases. This is due to its subsequent decomposition and is in good agreement with proposed theory. Data for the polymeric peroxides is omitted since this data could not be properly interpreted.

**Oxidation Run Procedure**

The first runs made with new variables were those with modifications in temperature and catalyst concentration. This enabled evaluation of variations on yield and catalyst activity. This series of runs utilized aqueous 49% HBr (Fisher Scientific) and cobaltacetate-tetrahydrate (Malinkrodt Analytical Reagent Grade). This afforded the
Figure 3. Organic Peroxide Content
presence of undesirable water. A second series of runs and a final series of runs were made under "anyhydrous conditions". The solvent, normally 250 ml glacial acetic acid (Fisher Scientific Reagent grade) was anhydrously prepared upon addition of 2 ml of acetic anhydride (Fisher Scientific Reagent grade) twenty-four hours prior to its use. The catalyst consisting of a metal acetate and halogen salt was prepared by drying the metal acetate and halide salt at 135°C for 48 hours under a 30 inch vacuum. These were dried in respective 125 ml ground glass Erlenmeyer flasks, labeled and stoppered.

A 9.2% solution of anhydrous HBr in acetic acid, another halogen promoter was prepared by addition of 26.3 grams of anhydrous HBr (Fisher Scientific) to 259.4 g of slowly stirred glacial acetic acid.

At the beginning of each run, the dry ice condenser and the cold trap were charged with dry ice and acetone. The reaction flask was then charged with 250 ml glacial acetic acid solvent and the air stirrer was slowly started. The catalyst was then added and the solution was heated to reaction temperature under a 20.0 ml per minute dry nitrogen purge until the catalyst had dissolved. The temperature of the reaction mixture was regulated via a variable transformer and an ice bath. This procedure involved simply removing the heating mantle and replacing it with the ice bath or vice-versa, both dependent upon whether heating or cooling was desired.

When the catalyst had dissolved the mixture was cooled to approximately 38°C-40°C. The gas inlet tube was removed and the
piperylene was added. The gas inlet tube was reinserted and the mixture was heated to reaction temperature again under nitrogen. After the temperature stabilized, the N₂ purge was stopped. The stirrer was speeded up and a flow of oxygen (Airco, Inc., 99%) was started with the time being recorded. The O₂ flowrate was adjusted to the desired flow rate via the inlet needle valve and the O₂ absorption was monitored via the outlet rotameter. Both the inlet and the outlet flow were recorded periodically.

Initially a 5.0 ml sample was taken from the reaction mixture just prior to the start of oxygen flow. As the run progressed, 5.0 ml samples of the reaction mixture were withdrawn from the sample port and analyzed on the gas chromatograph. Samples were generally taken at 10 or 15 minute intervals. Run times were generally limited to 45 minutes to one hour to minimize loss of catalyst activity and product yield.
RESULTS AND DISCUSSION

Series I

In this first series of runs, water was present at the start of the reaction. The catalyst system consisted of cobalt acetate tetrahydrate and 48% aqueous hydrobromic acid. The solvent used was glacial acetic acid. The amount of catalyst, the oxygen flow and the temperature were varied.

In general, the yields of 2,4-pentadienoic acids which are listed in Table VII were markedly lower than were obtained in later runs where an initially anhydrous system was used. It can be noted that yields appear to increase with temperature, catalyst concentration and decrease with the bromide/cobalt ratio.

As judged by the gas chromatogram, a large number of products were formed. This lack of selectivity increased at lower temperatures with a greater production of high retention time products. All runs in this series resulted in an approximately 98.6% conversion.

Series II

Tables VIII and IX summarizes the results obtained for runs in which initially anhydrous conditions were employed.

The data from the runs utilizing metal acetates in the absence of bromide ion indicate that the presence of bromide ion is vital for rate enhancement as well as product formation. Cobalt salts were found to yield some product without the aid of the halide promoter, however the reaction was substantially slower. In contrast, manganese
## TABLE VII

Results for CoAc₂·4H₂O - 48% HBr(aq)

<table>
<thead>
<tr>
<th>Run</th>
<th>1,3 Diene</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Max O₂ flow</th>
<th>Temp°C</th>
<th>Max Yield</th>
<th>% Conv.</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2075 moles 83% diene</td>
<td>glac HAC 250 ml</td>
<td>Co⁺² 0.20M Br⁻ 0.20M</td>
<td>---</td>
<td>85</td>
<td>60</td>
<td>99.1</td>
<td>12.0%</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Co⁺² 0.20M Br⁻ 0.20M</td>
<td>200</td>
<td>60</td>
<td>60</td>
<td>99.50</td>
<td>7.8%</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Co⁺² 0.20M Br⁻ 0.40M</td>
<td>200</td>
<td>90</td>
<td>60</td>
<td>99.0</td>
<td>4.2%</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Co⁺² 0.20M Br⁻ 0.040M</td>
<td>140</td>
<td>85</td>
<td>60</td>
<td>98.6</td>
<td>3.4%</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Co⁺² 0.020M Br⁻ 0.020M</td>
<td>140</td>
<td>85</td>
<td>60</td>
<td>96.2</td>
<td>5.5%</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Co⁺² 0.20M Br⁻ 0.20M</td>
<td>100</td>
<td>85</td>
<td>60</td>
<td>98.6</td>
<td>14.0%</td>
</tr>
</tbody>
</table>
### TABLE VIII

Results for Anhydrous Catalyst and Solvent

<table>
<thead>
<tr>
<th>Run</th>
<th>1,3 Diene</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Max O₂ flow (ml/min)</th>
<th>Temp °C</th>
<th>Max Yield</th>
<th>% Conv.</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>.2075 moles</td>
<td>glac HAC</td>
<td>CoAc₂</td>
<td>9.2% HBr in HAC</td>
<td>140</td>
<td>85</td>
<td>99.2</td>
<td>10.8%</td>
</tr>
<tr>
<td>7</td>
<td>83% diene</td>
<td>250 ml</td>
<td>0.20M</td>
<td>0.20M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>glac HAC</td>
<td>&quot;</td>
<td>KBr</td>
<td>100</td>
<td>85</td>
<td>99.4</td>
<td>18.0%</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>250 ml</td>
<td>&quot;</td>
<td>0.20M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>&quot;</td>
<td>CoAc₂</td>
<td>NaBr</td>
<td>200</td>
<td>85</td>
<td>99.1</td>
<td>23.5%</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>&quot;</td>
<td>0.13M</td>
<td>0.40M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>&quot;</td>
<td>CoAc₂</td>
<td>9.2% HBr in HAC</td>
<td>200</td>
<td>85</td>
<td>99.3</td>
<td>10.4%</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>&quot;</td>
<td>0.20M</td>
<td>0.20M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>&quot;</td>
<td>MnAc₂</td>
<td>KBr</td>
<td>200</td>
<td>85</td>
<td>93.6</td>
<td>14.8%</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>&quot;</td>
<td>0.20M</td>
<td>0.20M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>&quot;</td>
<td>CoAc₂</td>
<td>9.2% HBr in HAC</td>
<td>20</td>
<td>28</td>
<td>2 days</td>
<td>97.9</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>&quot;</td>
<td>0.14M</td>
<td>0.20M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>&quot;</td>
<td>MnAc₂</td>
<td>&quot;</td>
<td>100</td>
<td>85</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>&quot;</td>
<td>0.14M</td>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>1,3 Diene</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Max O₂ flow</th>
<th>Max Yield</th>
<th>% Conv.</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Metal</td>
<td>Promoter</td>
<td>Temp °C</td>
<td>Time</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>.2075 moles</td>
<td>glac HAC</td>
<td>CoAc₂</td>
<td>---</td>
<td>200</td>
<td>85</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>83% diene</td>
<td>250 ml</td>
<td>0.04M</td>
<td></td>
<td>99.8</td>
<td>11%</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>&quot;</td>
<td>&quot;</td>
<td>CoAc₂</td>
<td>NaBr</td>
<td>200</td>
<td>85</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.13M</td>
<td>0.40M</td>
<td>98.5</td>
<td>34.9%</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>&quot;</td>
<td>&quot;</td>
<td>CoAc₂</td>
<td>&quot;</td>
<td>45</td>
<td>95.9</td>
<td>65.0%</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.04M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>&quot;</td>
<td>&quot;</td>
<td>MnAc₂</td>
<td>&quot;</td>
<td>40</td>
<td>92.9</td>
<td>63.1%</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.04M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>&quot;</td>
<td>&quot;</td>
<td>CoAc₂</td>
<td>&quot;</td>
<td>60</td>
<td>97.7</td>
<td>56.0%</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.020M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>.2075 moles</td>
<td>&quot;</td>
<td>CoAc₂</td>
<td>&quot;</td>
<td>45</td>
<td>97.9</td>
<td>70.2%</td>
</tr>
<tr>
<td></td>
<td>99% trans 1,3 diene</td>
<td></td>
<td>0.04M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>.2075 moles</td>
<td>&quot;</td>
<td>CoAc₂</td>
<td>KBr</td>
<td>&quot;</td>
<td>40</td>
<td>97.8</td>
</tr>
<tr>
<td></td>
<td>83% diene</td>
<td>&quot;</td>
<td>0.026M</td>
<td>0.40M</td>
<td></td>
<td>54.7%</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>&quot;</td>
<td>&quot;</td>
<td>CoAc₂</td>
<td>&quot;</td>
<td>&quot;</td>
<td>40</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.04M</td>
<td></td>
<td></td>
<td>81.0%</td>
<td></td>
</tr>
</tbody>
</table>
TABLE VIII

Results for Anhydrous Catalyst and Solvent (cont.)

<table>
<thead>
<tr>
<th>Run</th>
<th>1,3 Diene</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Max O₂ flow (ml/min)</th>
<th>Temp°C</th>
<th>Time</th>
<th>% Conv.</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>.2075 moles</td>
<td>glac HAC</td>
<td>CoAc₂</td>
<td>200</td>
<td>85</td>
<td>40</td>
<td>98.8</td>
<td>57%</td>
</tr>
<tr>
<td></td>
<td>83% diene</td>
<td>250 ml</td>
<td>KBr</td>
<td>0.04M 0.40M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## TABLE IX

Results for Variable 1,3-Pentadiene Purity and Anhydrous Solvent and Catalyst

<table>
<thead>
<tr>
<th>Run</th>
<th>1,3 Diene</th>
<th>Solvent</th>
<th>Metal [CoAc₂]</th>
<th>[MnAc₂]</th>
<th>[FeAc₂]</th>
<th>Promoter</th>
<th>Max O₂ flow (ml/min)</th>
<th>Temp°C</th>
<th>Time</th>
<th>% Conv. Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>.2075 moles</td>
<td>glac HAC</td>
<td>0.026M</td>
<td>---</td>
<td>---</td>
<td>NaBr</td>
<td>200</td>
<td>85</td>
<td>50</td>
<td>99.2 44%</td>
</tr>
<tr>
<td>24</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.032M 0.008M</td>
<td>---</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>60</td>
<td>99.4 52%</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.0132M 0.0132M</td>
<td>---</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Reflux</td>
<td>40</td>
<td>99.3 46%</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>&quot;</td>
<td>&quot;</td>
<td>--- --- 0.04M</td>
<td>NaBr 0.40M</td>
<td>100</td>
<td>85</td>
<td>10.5 hrs</td>
<td>80.1 5.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.004M</td>
<td>&quot;</td>
<td>NaBr 0.04M</td>
<td>200</td>
<td>85</td>
<td>50</td>
<td>98.4 14.2%</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>.2075 moles</td>
<td>&quot;</td>
<td>0.04M</td>
<td>&quot;</td>
<td>NaBr 0.40M</td>
<td>200</td>
<td>Reflux</td>
<td>50</td>
<td>100 35.3%</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>.2075 moles</td>
<td>&quot;</td>
<td>0.04M</td>
<td>&quot;</td>
<td>100</td>
<td>Comp.air</td>
<td>85</td>
<td>2.5 hrs</td>
<td>99.3 46%</td>
<td></td>
</tr>
</tbody>
</table>
salts in the absence of bromide ion displayed low solubility, slower oxygen absorption, and no product formation.

In most metal ion autoxidation systems the anion associated with the metal ion is of minor importance. Bromide is known to aid the solubility and possibly increases the oxidation-reduction potential of the metal ions involved. This behavior was observed in runs made in the presence of bromide under similar conditions as runs made in the absence of bromide resulted in a 65.1 percent yield for the cobalt acetate bromide catalyst system and a 63.1 percent yield for the manganese acetate bromide catalyst system. This is compared to an 11 percent yield for the cobalt system and 0 percent yield for the manganese system in the absence of bromide ion (runs 13 and 14 versus 16 and 17). In addition to a higher yield of product for runs made in the presence of bromide, an increased solubility of the metal salts in the solvent and an increased oxygen absorption rate was observed.

Anhydrous sodium bromide and potassium bromide were found to be better promoters than anhydrous or aqueous hydrogen bromide when used in conjunction with cobalt acetate and manganese catalyst systems discussed above.

A ferric acetate-acetate catalyst system promoted by sodium bromide was investigated. This proved to be a poor catalyst as a very slow oxygen absorption rate and low yield resulted. This run (26) gave the lowest conversion of 80.1% of all runs made, poor selectivity, and required ten and one half hours to reach a maximum yield of 5.1%.

Cobalt acetate and manganese acetate mixed catalyst systems
were found to give a fair yield but required a longer reaction period of sixty minutes in comparison to forty-five minutes for other runs made with similar catalyst concentrations. Another observation from the results obtained in runs 8, 15, 16 and 18 concerns the ratio of bromine atoms to the atoms of cobalt in the catalyst system and the molar concentration of the metal ion. Figures 4 and 5 graphically show these effects. It is noted that as the ratio of bromide to cobalt increases, the yield increases and that an increase in the amount of catalyst tends to decrease the yield of the desired product. All of these results were obtained at a constant temperature of 85°C.

An oxygen absorption curve is given in Figure 6 for a typical run (7). The rate of oxygen absorption increases quite rapidly to a maximum at about 25 minutes and then continuously decreases during the remainder of the run. The time maximum yield of product is approximately 45 minutes and the average degree of conversion for most runs is approximately 98.6 percent. These results are also given in Figure 6.

The use of compressed air (run 29) gave a reasonable yield of 45%. This reaction however required a longer reaction period of two and one half hours for a maximum product formation at an impressive 99.3% conversion of the 1,3-pentadiene. It was initially thought that the large amount of inert nitrogen present in the air would "sweep" the substrate through the reactor and into the diene trap. This was not observed as no diene was present in the trap upon completion of the run.
Figure 4. Effect of Bromide ion to Cobalt ion on Yield
Figure 5. Effect of amount of catalyst on yield
Figure 6. Oxygen absorption rate, % conversion of 1,3 pentadiene and % yield 2,4 pentadienoic acid as a function of time for a typical run (Run #7)
Finally, from these results there is an indication of a relationship between substrate purity and product yield, a 99% pure trans piperylene fraction (Aldrich Company) resulted in a 70% yield and a much cleaner reaction according to gas chromatography analysis. The maximum yield obtained for the 83% piperylene fraction utilized in most runs was 65%. In contrast, a C₅ cut containing a 46% mixture of cis and trans piperylenes resulted in a 35% yield. This represents a 50% reduction in product yield when compared to the pure trans piperylene fraction run and according to gas chromatography analysis a more complex reaction mixture. It is also noted that as the purity of the substrate decreased, a longer reaction period was required for maximum yield to occur.
CONCLUSIONS

Examination of these results obtained in this project leads to the following conclusions:

(1) The apparent low yields obtained from runs made in the presence of water make this condition a very weak candidate for future oxidations of this type.

(2) Anhydrous conditions of solvent and catalyst at a constant temperature of 85°C results in maximum yields.

(3) A high bromide ion concentration is necessary for the formation of the desired 2,4-pentadienoic acid product. The order of halide activity with increasing yield is approximately NaBr > KBr > HBr.

(4) The yield increases as the ratio of atoms of bromine to atoms of cobalt increases with a corresponding reduced amount of metal ion in the overall molar concentration of the catalyst.

(5) The cobalt acetate bromide catalyst system is the best catalyst system for utilization in this oxidation followed by manganese acetate bromide. The manganese acetate bromide catalyst system however, presents solubility problems within the reaction mixture.

(6) A mixed cobalt-manganese acetate catalyst system has no advantage over cobalt alone.

(7) Iron is a very poor catalyst for this oxidation.

(8) Compressed air can be used as a substitute for gaseous oxygen but results in a lower yield and longer reaction time.

(9) The fact that higher yields and less by-product formation occurred
with the purer substrate indicate that there is a strong dependency on substrate purity for the desired product.

(10) The reaction system and the operating procedure led to rapid, convenient and reproducible oxidations. It is suggested that this method be applied to simpler alkenes which might result in a greater selectivity.
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(76) Valentine, J. S. (1973), Chem. Rev. 73, 235.


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