CHAPTER 4

OXIDATION OF PARAFFINS
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4.1 Introduction

Engler\(^1\) showed the possibility of obtaining fatty acids from higher paraffins. The industrial application of paraffin oxidation\(^2,3\) was carried out by oxidizing paraffins with air at 130 to 135°C to win fatty acids. Kelber mentioned the usage of manganese compounds as catalysts\(^4\) for paraffin oxidation. The technology and technical aspects\(^5,6\) of paraffin oxidation of particular unbranched paraffins of C\(_{20}\) to C\(_{35}\) at 120°C in the presence of manganese salts were described. Oxidation of medium chain paraffins of C\(_{10}\) to C\(_{18}\) lead to the production of the secondary alcohols\(^7,8\) with the corresponding chain lengths which were subjected further to obtain non ionized Tensides.

4.2 Hydroperoxide formation and C-H bond reactivities

Rieche predicted the formation of alkylhydroperoxide\(^9\) as the primary product of the oxidation of paraffins. Ivanov isolated\(^10\) the corresponding hydroperoxide in the oxidation of n-heptane. As the kinetic chain length of paraffins by autoxidation is generally lower than 5, the yield of the hydroperoxide in the primary step of the oxidation is considerably lower than 100%. Besides the hydroperoxide, alcohols and ketones corresponding to the chain termination between secondary peroxyradicals\(^11\) are also expected. It is concluded that by relatively lower temperatures of 100-120°C, the oxidation of n-paraffin takes place preferably through hydroperoxide. But at higher reaction temperatures, the importance of hydroperoxide decreases due to increase in the rate of initiation and decrease of the kinetic chain length because the peroxyradicals under chain termination react to give alcohols and ketones to a great extent. The same alcohols and ketones are formed generally as secondary products when the hydroperoxides undergo decomposition.
Autoxidation could be a good method for cetane number improvement\textsuperscript{12} of diesel and kerosene due to the hydroperoxides produced. Alkanes having a lower carbon number produced more hydroperoxides because the hydroperoxide concentration of the alkane is dependent on both its hydroperoxide production ability and its molecular weight. The autoxidation mechanism is generated as (Scheme 1).

**Initiation**

\[\text{OOH} \xrightarrow{R-H} \text{R}^* \quad (\text{Rate} = k_1)\]

**Propagation**

\[\text{R}^* + \text{O}_2 \rightarrow \text{ROO}^*\]
\[\text{`QOOOH} + \text{O}_2 \rightarrow \text{`OOQOOH}\]
\[\text{ROO}^* + \text{RH} \rightarrow \text{ROOH} + \text{R}^*\]
\[\text{`OOQOOH} + \text{RH} \rightarrow \text{`QOOH}\]
\[\text{`OOQOOH} \rightarrow \text{O=CR`OOH} + \text{HO}^* \rightarrow \text{R}^*\]

**Termination**

\[\text{`OOQOOH} + \text{`OOQOOH}\]
\[\text{`OOQOOH} + \text{ROO}^* \rightarrow \text{Non-Radical, Non Hydroperoxide}\]
\[\text{ROO}^* + \text{ROO}^*\]

**Scheme 1:** Autoxidation Mechanism of Hydrocarbons

Rate parameters for nine type of reactions, which are supposed to be important in the low temperature chemistry of alkane oxidation\textsuperscript{13-15} were reported. The conversion of alkanes to oxygen-containing compounds with molecular oxygen catalyzed by transition
metal\textsuperscript{16} is one of the most important and fundamental transformation in industrial chemistry\textsuperscript{17,18}.

If the oxidation is carried out in the presence of the typical oxidation catalysts e.g. Mn or Co salts, the peroxides formed can be iodometrically estimated as the isolation is not possible because of the presence of the catalysts, the hydroperoxide decomposition is favoured. By paraffin oxidation processes in short reaction times and in lower turnovers, alcohols and ketones with unchanged carbon chain are preferably obtained.

Ivanov\textsuperscript{10} considered the isolated hydroperoxide from the heptane oxidation mixture as 2-hydroperoxyheptane. Przikow and co-workers concluded that all secondary hydroperoxy heptanes were formed in relatively comparable amounts. It was also shown that all the secondary C-H bonds present in different positions were attacked with almost the same reaction velocities. The exact data about the relative reaction rates of C-H bonds at different positions for the oxidation of n-decane was shown by Benton and Wirth\textsuperscript{19}. The results obtained by I.R. spectroscopy were confirmed in many cases by gas chromatographic methods\textsuperscript{20-22}.

A secondary C-H bond was 10 to 20 times easily attacked than a primary C-H bond. The reactivity of the secondary C-H bond at 2\textsuperscript{nd} position was slightly more reactive than the one at 3\textsuperscript{rd} position. The reactivity of the secondary C-H bond decreases as its distance increases from the chain end of the paraffin. This follows in general the regularity shown in radical substitutions of n-paraffins\textsuperscript{23}.

Alkyl peroxy radical formed as intermediate by the primary attack on C-H bond of a paraffin can react preferably with a C-H bond of another molecule of the paraffin intermolecularly and also intramolecularly.

\[
\begin{align*}
R-\text{CH}_2\text{CH}-\text{CH}-\text{R} & \quad \text{CH}_2\text{CH}-\text{CH}-\text{R} \\
& \quad \text{H} \quad \text{O} \\
\end{align*}
\]
Such intramolecular C-H bond cleavages through peroxy radicals appear in the case of autoxidation of ditertiary paraffins when the tertiary C-H bonds are present in 1,3-position with respect to each other. Oxidation of alkanes catalyzed by Fe₂(μ-carboxylato) complexes show stereospecific transfer²⁴ of an oxygen atom from H₂O₂ to C-H bonds in alkanes. The C-H bond cleavage in the intermediate peroxyl radicals is possible due to its rearrangement to a six-member transition state²⁵. The intramolecular hydrogen atom abstraction in the intermediate peroxyl radicals can only take place to a less extent in the oxidation of n-paraffins. The reaction must also lead to the formation of bifunctional compounds like dihydroperoxide, hydroperoxy alcohols, hydroperoxy ketones, diketones etc. The composition of such bifunctional products with unchanged hydrocarbon rest is very low in the case of paraffins of C₅-C₁₆. The intramolecular hydrogen atom abstraction is shown possible in general in the case of the peroxyl radicals formed in n-paraffin oxidation. The ratio of intramolecular hydrogen atom abstraction to intermolecular abstraction is shown to be between 0.1 to 0.2, although it is greater for n-hexadecane than n-pentane. The ratio increases with increase of temperature.

While Rieche⁹ presumed that the hydroperoxides formed in the paraffin oxidation as primary products undergo decomposition through the cleavage of the carbon chain, Langenbeck and Pritzkow²⁶-²⁹ came to a conclusion on the basis of the examination of the oxidation of alcohols and Tetralin³⁰ that the decomposition of secondary hydroperoxides preferably leads to the formation of the ketones and alcohols.

$$\begin{align*}
R'CH-OH \quad \rightarrow \quad R'-CHO + R'-OH
\end{align*}$$

This conclusion is further established experimentally³¹ in the oxidation of n-pentane, n-hexane, n-heptane and n-decane. At high temperatures during the decomposition of the secondary hydroperoxide, the fragmentation of the alkoxy radical formed as intermediate also takes place³².

$$\begin{align*}
R'CH-O' \quad \rightarrow \quad R'-CHO + R'
\end{align*}$$
As a result of this, the corresponding hydrocarbon R'-H and R'-OH form. The degree of the ratio of fragmentation to total reaction is very low below the temperatures of 150°C or under the normal conditions of the paraffin oxidation. By kinetic isotopic methods, decane hydroperoxide decomposition under the conditions of the oxidation at 150°C lead to 55% of the hydroperoxide to ketones, 26 to 30% to secondary alcohols and 11 to 18% to lower alcohols and lower carboxylic acids. The presence of lower primary alcohols in the products of the oxidation of paraffins is doubtless due to the fragmentation of the secondary alkoxy radicals. The decomposition of the primarily formed hydroperoxide can be enhanced through transition metal salts and complexes. The order of activity is generally Co > Mn > Cu > Ni > Fe ≥ Zn. In the absence of oxygen more alcohols than ketones are formed although under normal conditions of paraffin oxidation, more ketones than the alcohols are formed as the alcohols formed are further oxidized to ketones. Therefore at 120°C in the absence of catalysts and also with Mn or Co salts about 60% ketones and 40% alcohols were formed although slightly more ketone were formed with Cr salts.

4.3 Further oxidation of hydroperoxide-decomposition products
Alcohols and ketones formed primarily by the chain termination and by the decomposition of the hydroperoxides are oxidized further with higher rates. Their rate of oxidation is more than that of the starting paraffin. In the case of the oxidation of n-decane, n-decanol was attacked 6 times more than n-decane. In generally, the rate of paraffin oxidation proceeds as in the case of the oxidation of cyclohexane i.e. starting paraffin < ketone < alcohols.

The oxidation of secondary alcohols leads mainly to ketones. Alcohols formed by the fragmentation reactions are oxidized to carboxylic acids via aldehydes. It should be taken into consideration that if the attack takes place at the non activated secondary C-H bonds of the alkyl rest with comparable rate like the attack to the -OH group attached geminal C-H bonds, not only the carboxylic acids with the same number of carbon atoms but also hydroxy acids with shorter carbon chain length can form. The
oxidation of alcohols to ketones were studied thoroughly on model substances like isopropanol\textsuperscript{16} and cyclohexanal\textsuperscript{17}. In the absence of catalysts, one obtains the corresponding compounds and hydrogen peroxide most likely via the hydroperoxyalkylhydroperoxides.

\[
\begin{align*}
R{\text{CH-OH}} + O_2 & \rightarrow R\text{C-OH} \\
& \rightarrow R\text{C-O} + H_2O_2
\end{align*}
\]

The hydroxyalkylhydroperoxide can also undergo decomposition through cleavage of O-O peroxide bond to give the radical which in turn undergoes fragmentation easily.

\[
\begin{align*}
R\text{C-OH} & \rightarrow R\text{C-OH} + R^n
\end{align*}
\]

This reaction shall take place much easily in the presence of catalysts. The significance of this fragmentation under the conditions of paraffin oxidation is not well known and indeed it should be considered that this reaction is jointly responsible for the formation of lower alcohols in paraffin oxidation besides fragmentation by the decomposition of the secondary alkyl hydroperoxides. Further oxidation of the ketones takes place through $\alpha$-hydroperoxy ketones\textsuperscript{38-40} formed by radical chain reaction. The $\alpha$-hydroperoxy ketones decompose to aldehydes and carboxylic acids under acid catalysis\textsuperscript{41,42}, thermal\textsuperscript{43,44} conditions or catalysis through transition metals\textsuperscript{45}.

\[
\begin{align*}
\text{RCH}_{2} + O_2 & \rightarrow \text{RCH-OOH} \\
& \rightarrow \text{CHO} \quad \text{RCH}_{2} + O_2 & \rightarrow \text{RCH-OOH} \\
& \rightarrow \text{COOH}
\end{align*}
\]

Hock rearrangement is a special case of the acid catalyzed decomposition. Surprisingly, it takes place even in the presence of carboxylic acids\textsuperscript{41,42}. The probable mechanism of the decomposition should be through ionic fragmentation.
The decomposition of pure, crystalline $\beta,\beta$-diphenylpropionmesitylene hydroperoxide\(^{46}\) in methanol under the influence of benzoic acid gave free mesitylene carboxylic acid but not mesitylene carboxylic methyl ester. By the ionic fragmentation as shown above, the acyl cation must give the corresponding methyl ester with the nucleophilic solvent methanol.

The decomposition of $\alpha$-hydroperoxy ketones in thermal and through the transition metal compounds proceeds via radical fragmentation.

This reaction is responsible for the formation of considerable amounts of carbon monoxide and the consecutive products of the alkyl radical $R'$ i.e. $R'$-$H$, $R'$-$OH$ in the decomposition of $\alpha$-hydroperoxy ketones with Co or Mn-salts.

When the oxidative attack of the ketones takes place at $\alpha$-position and not at other positions and also on not activated C-H bonds, the rate of oxidation of ketones is independent of the chain length. In reality, the oxidisabilities $\frac{k_P}{\sqrt{2k_h}}$ of a large number of $C_5$ to $C_{10}$ ketones are in accordance within the limits\(^{47}\) of error. The findings correspond to the experimental results of the oxidation of $C_5$ to $C_{13}$ ketones which gave 70 to 90% carboxylic acids as expected due to selective attack at $\alpha$-position and 10 to 30% carboxylic acids with lower carbon chain length. It is known that the carboxylic
acids with lower carbon chain length are obtained to an extent of 10 to 30% due to oxidation of non activated (non α-position) C-H bonds.

It is established\textsuperscript{48} that the products of the oxidation of higher ketones contain not only aldehydes and monocarboxylic acids as well as the bifunctional compounds with unchanged carbon framework but also γ-lactones, lactides and estolides. These findings were confirmed by Rif\textsuperscript{49} et al. The presence of γ-lactones were identified by I.R. and gas chromatographic methods. The formation of hydroxy acids can be explained via the trifunctional oxidation products with unchanged carbon atom framework which form from peroxyradicals through intramolecular radical C-H bond cleavage.

\[
\begin{align*}
\text{R-CO-CH}_2\text{CH-R'} & \rightarrow \text{R-CO-CH}_2\text{CH-R'} + \text{HOOC-CH}_2\text{-CH-R'} \\
\text{O} & \rightarrow \text{OOH} & \text{O} & \rightarrow \text{OOH}
\end{align*}
\]

This is of course can not be a general mechanism because through these routes only β-hydroxy carboxylic acids can form. It must be established that surely the esters are formed by the oxidation of ketones. Methylethyl ketone yielded at 100°C besides acetic acid mainly ethyl methanoate\textsuperscript{50}. This is the likely pathway of the formation of ethyl methanoate in the oxidation of n-butane\textsuperscript{4}.

Ethyl methanoate could be formed from methylethyl ketone through Baeyer-Villiger oxidation\textsuperscript{51,52} with peracetic acid.

\[
\begin{align*}
\text{CH}_3\text{-CO-CH}_2\text{-CH}_3 + \text{CH}_3\text{-C-O-OH} & \rightarrow \text{CH}_3\text{-CO-O-CH}_2\text{-CH}_3 \\
& + \text{CH}_3\text{-COOH}
\end{align*}
\]

Baeyer-Villiger reaction was shown responsible for the formation of ε-caprolactam in the oxidation of cyclohexane. The reaction takes place very slowly with higher aliphatic ketones than cyclohexanone and therefore the importance of this reaction
in the oxidation of paraffins is disputed. A sure evidence for another radical reaction mechanism through which an ester formation by the oxidation of ketones e.g.

$$R'\text{--CO--R}^\cdot + R\text{--O--O}^\cdot \rightarrow R'\text{--CO--O--R}^\cdot + RO^\cdot$$
could not be considered.

Further oxidation of aldehydes formed by the decomposition of α-hydroperoxy ketones but also by the radical fragmentation of alkylhydroperoxides lead to the formation of the corresponding carboxylic acids\textsuperscript{53} via peracids.

$$\text{R--CH}_2\text{--C--H} + \text{O}_2 \rightarrow \text{R--CH}_2\text{--C--OOH}$$

$$\text{R--CH}_2\text{--C--OOH} + \text{R--CH}_2\text{--C}^\cdot \rightarrow 2\text{R--CH}_2\text{--C--OH}$$

The first step of this reaction takes place by radical mechanism with large kinetic lengths ($\gamma = 100$ to 1000)\textsuperscript{54-56} while the second step is an ionic one taking place through an adduct from peracid and aldehyde\textsuperscript{57}.

$$\text{R--CH}_2\text{--C--H} + \text{R--CH}_2\text{--C--OOH} \rightarrow \text{R--CH}_2\text{--C--O--O--CH--CH}_2\text{--R}$$

The intermediate acyl radical which form by the radical oxidation of aldehydes can react not only with oxygen but also can undergo decarbonylation\textsuperscript{58}.

$$\text{R--CH}_2\text{--C}^\cdot + \text{OH--C--CH}_2\text{--R} \rightarrow \text{R--CH}_2\text{--C--O--C--CH}_2\text{--R + H}^\cdot$$
The decarbonylation but also the radical decarboxylation of peracids\textsuperscript{59-61} and the attack

\[
\text{R-CH}_2\text{C-O-OH} \rightarrow \text{R-CH}_2\text{C}' \rightarrow \text{R-CH}_2' + \text{CO}_2
\]

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

at the activated \text{-CH}_2\text{ group at } \alpha\text{-position is responsible in the oxidation of aliphatic}

aldehydes not only for the formation of the corresponding carboxylic acids but also the

compounds (e.g. hydrocarbons, alcohols, aldehydes, carboxylic acids.) with one carbon

atom less in the carbon chain. The share of the radical decarbonylation as well as the

radical decarboxylation increases with the increase in the temperature.

It is known that acid anhydrides\textsuperscript{62} can be formed by the oxidation of aldehydes.
The deciding reaction step here is the oxidation of the intermediate acyl radical which

takes place through the transition metal ions especially through Cu-ions. Whether this

reaction is possible under the conditions of the oxidation of paraffins is not surely

evident.

The reaction could explain the formation of esters but it should be taken into

consideration that for the formation of acid anhydride, the especially effective Cu-
catalysts are not generally employed in the oxidation of paraffins. Carboxylic acids are

mostly the end products of the paraffin oxidation. But they undergo further oxidation. It

is understandable that their C-H bonds atleast which are nearer the carboxylic group

should possess the reactivity comparable with the oxidation of C-H bonds in n-paraffins.
The authors initially engaged with the oxidation of carboxylic acids considered a

preferential oxidation on C-H bonds at \beta-position\textsuperscript{62}. Berezin supported the \beta-oxidation

observations by taking the \textsuperscript{14}C-labelled carboxylic acids where \textsuperscript{14}CO\textsubscript{2} is cleaved off. But

later it was established that carboxylic acids under the conditions of autoxidation

according to the equations,
\[
\begin{align*}
&\text{R-COOH} + \text{R'-O-O} \rightarrow \text{R-C-O'} + \text{R'-OOH} \\
&\text{R-C-O'} \rightarrow \text{R'} + \text{CO}_2
\end{align*}
\]
decarboxylate and therefore one can’t conclude that the formation of \(^{14}\text{CO}_2\) in the autoxidation of \(^{14}\text{C}\)-labelled carboxylic acid is due to \(\beta\)-oxidation only. Pritzkow\(^{63}\) showed that capric acid methylester was attacked at all secondary C-H bonds by molecular oxygen and there was no preference for \(\beta\)-C-H attack. From the statistics of the attack at C-H bonds it was shown that the velocity of oxidation decreases with increase in the chain length of the carboxylic acids. The reactivity differs in the same way as in the case of primary, secondary C-H bonds in n-paraffins or in ketones.

4.4 Formation of esters in the oxidation of n-paraffins

In the oxidation of n-paraffins, besides free carboxylic acids, esters were also reported in the oxidates to the extent of 50 to 70% of the total free acids\(^ {64}\). A part of the esters like lactones and lactides could be removed by saponification of the paraffin oxidation mixture with NaOH. Lactones and respectively the hydroxyacids responsible would form through the oxidation of ketones. They should also be expected as products of oxidation of secondary alcohols when the attack doesn’t take place at the C-H bond to which the \(-\text{OH}\) group is attached as well as products of further oxidation of carboxylic acids.

The follow up of the ester and acid content during the oxidation of n-paraffins show that ester and acids form side by side from the beginning. Consequently esters are not the consecutive products of the conversion of the carboxylic acids formed in the paraffin oxidation with the secondary alcohols formed at the same time. Indeed the reaction rate of carboxylic acids with secondary alcohols under the conditions of paraffin oxidation is so low that this reaction doesn’t have a considerable part in the formation of esters\(^ {65}\).

Langenbeck and Pritzkow considered that the ester formed in the paraffin oxidation could be due to Baeyer-Villiger reaction of the ketones with peracids, both formed as intermediates. This reaction is indeed relatively slower in the case of high
molecular weight open chain ketones and therefore it is questionable whether this reaction has considerable part for the formation of esters in the oxidation of n-paraffins. There is no proof for Berezin formulated radical oxidation of ketones to esters and also the formation of intermediate acid anhydride is not established and therefore it should be seen that the formation of a true ester in the paraffin oxidation is not clear. But it is sure that true esters are formed besides lactones and lactides.

4.5 Composition of carboxylic acids from the paraffin oxidation

Normally the monocarboxylic acids are the aspired products of paraffin oxidation. By statistical attack at secondary C-H bonds of the paraffin employed and in the case of selective further oxidation of reaction's intermediate products (e.g. alcohols at geminal, ketones at the α-positioned C-H bonds), one expects that the carboxylic acids with medium chain length form around 50% of the starting hydrocarbon. By the oxidation of Cₙ paraffins, the carboxylic acids C₃ to Cₙ₋₂ should form in comparable amounts and the carboxylic acids Cₙ₋₁ to Cₙ should form in lower amounts (as it is formed only by the oxidation of a methyl group). Formic acid is expected to form in considerable amounts when the aldehyde formed as intermediate undergoes oxidation of the C-H bonds at α-position.

Grüns⁵ conclusions that although all carboxylic acids from C₁ to Cₙ are formed, the ones with lower carbon chain lengths predominate were further established⁶⁶,⁶⁷. The complete analysis of the carboxylic acids formed in the paraffin oxidation is highly difficult as the acids with less than C₄ are water soluble liquids. It is sure that the mole quantities of formic acid and acetic acids are more than the other acids. The effect of the catalysts employed is not perceptible. This points to the fact that by lower turn overs, the further oxidation of the carboxylic acids formed has no remarkable significance. The yield of higher acids from Cₙ₋₄ against the lower acids decreases considerably. It is not because that these acids are oxidized further at higher velocities but because that those intermediate products responsible for the formation of higher acids are relatively easily converted to higher functional oxidation products. A further oxidation of monocarboxylic acids is naturally possible and by high turn overs it commands significantly on the
distribution of the monocarboxylic acids. One finds the corresponding dicarboxylic acids further in the products of the technical paraffin oxidation$^{68}$ and they can be obtained as main products by increasing the turnovers. The processing of the reaction mixtures becomes very difficult as the paraffin oxidation is not employed to synthesis dicarboxylic acids. Besides the homologous fatty acids and dicarboxylic acids formed from the former, hydroxy acids (partly converted to lactones or lactides) and keto acids are also present in the reaction mixtures of paraffin oxidation. The complete analysis of these compounds is extraordinarily difficult and therefore not yet possible. The Varrentrapp reaction is responsible for the formation of monocarboxylic acids in the case of hydroxy acids.

\[
\begin{align*}
& \text{R} \text{CH}_2 \text{CH}-(\text{CH}_2)_n \text{COO}^- \\
& \text{OH}^- \rightarrow \text{R} \text{CH} \equiv \text{CH}-(\text{CH}_2)_n \text{COO}^- \\
& \text{OH}^- \rightarrow \text{R}-(\text{CH}_2)_n \text{CH}=\text{CH} \text{COO}^- \\
& \text{OH}^- \rightarrow \text{R}-(\text{CH}_2)_n \text{COO}^- + \text{CH}_3\text{COO}^- + \text{H}_2
\end{align*}
\]

4.6 Selective oxidation

A considerable urgency to replace the technologies with more efficient alternatives using dioxygen, hydrogen peroxide or other easily accessible and environmentally friendly oxidants for the conversion of petroleum products to valuable commodity chemicals$^{69}$ is in the offing. An integrated multistep process for selective partial oxidation of alkanes to alcohols, ethers or alkenes that provides unprecedented product control using dioxygen as the ultimate oxidant in a sequential zone flow reactor, an unique$^{70}$ approaches$^{71,72}$ with strong economic rationles$^{73-75}$ has come into focus with. The overall transformation is represented as (Scheme 2)
Scheme 2. Selective oxidation of alkanes to alcohols

There is the possibility of using alkanes directly by the petrochemical industries as they are more economical and less toxic as compared to aromatics.

The oxidation of n-butane to maleic anhydride has been commercialized\textsuperscript{76}. Selective oxidation and oxidehydrogenation of paraffins\textsuperscript{77-80} have been far from industrial interest as low yields of the final products are frequently observed due to

1. The reactivity of the product of partial oxidation is more than the starting hydrocarbon

2. Irreversible deactivation of the catalyst. In addition to the problems associated with the presence of consecutive reactions of oxidative degradation upon desired product and the undesired contribution.

Acetic acid, propanoic acid and solvents such as esters and lower ketones were industrially produced from butane\textsuperscript{81} and light gasoline\textsuperscript{82}. The mechanism using metalloprophyrins\textsuperscript{83} involves the hydrogen atom abstraction from the substrate, R-H by a
reactive iron-oxo intermediate followed by rapid transfer of the metal-bound oxygen atom to an intermediate caged alkyl radical.

Selective oxidation and functionalization of alkanes under mild conditions is an exciting scientific and economic goal\textsuperscript{83}. Selective formation of cyclohexyl hydroperoxide from cyclohexane is achieved in the presence of hydrogen peroxide dinuclear iron(III) complex\textsuperscript{84} with $\mu$-alkoxo bridges. Hydroperoxide formation\textsuperscript{85} based on MOPAC (AM1) calculations\textsuperscript{86} are available (Fig.).

![LUMO and HOMO of n-octane](image)

The catalytic activity of the polymer-bound Mn(IV)-triazacyclononane derivative system containing H$_2$O$_2$ and CH$_3$COOH was proved to be efficient in the oxidation of alkanes\textsuperscript{87,88} leading to the formation of corresponding alkyl hydroperoxides.

Pthalimide N-oxyl (PINO) radical, generated from N-hydroxy pthalimide (NHPI-carbon radical producing catalyst) abstracts a hydrogen atom from the carbon-hydrogen bond of various hydrocarbons including alkanes, alcohols, ethers, acetals and aldehydes under mild conditions, and forms the corresponding carbon radical with high selectivity and high catalytic efficiency\textsuperscript{89,90}. Cyclohexane is oxidized to adipic acid in one step with dioxygen (1 atm) by using NHPI compound with a small amount of Mn complex\textsuperscript{91}. 

\[
\text{C} + O_2 \xrightarrow{\text{NHPI Mn (acac)$_2$}} \text{COOH}_{\text{COOH}}
\]

\text{AcOH, 100°C}
A novel $O_2$ insertion into a Pt(IV)-hydride bond to form a stable Pt(IV) hydroperoxide compound is significant as the reactant is a Pt(IV) alkyl hydroperoxide complex\textsuperscript{92} analogous to those produced via oxidative addition of alkane C-H bonds thus promising for the development of commercially viable homogenous catalytic alkane oxidation. A dual mechanistic pathways involving predominantly a metal based oxidant proceeding in a heterolytic manner was proposed (Scheme 3) by Tembe et al.\textsuperscript{93,94} in the oxidation of cyclohexane by tert-butyl hydroperoxide using polynuclear manganese(III) Schiff base complexes.

\textbf{Scheme 3.} Mechanism for the oxidation of cyclohexane

Highly effective oxidation of alkanes by tert-butylhydroperoxide\textsuperscript{95} or peracetic acid\textsuperscript{96} in the presence of low-valent rhenium catalysts and the aerobic oxidation\textsuperscript{97} in the presence of Ru, Fe & Cu catalysts are known. Intermediacy of oxo-ruthenium\textsuperscript{98,99} rather than alkoxy radical was proposed.
A large number of reactions catalysed by transition metal containing catalysts involving coreductants and without couldn’t add till date anymore successful commercial process\textsuperscript{16} to the existing one i.e. the conversion of n-butane to maleic anhydride.

4.7 Oxidation under irradiation

Saturated hydrocarbons such as cyclohexane, n-hexane, propane, adamantane, cumene etc, were oxidized in the presence of dioxygen by a neutral luminescent trans-dioxoosmium(VI) complex under UV-Vis irradiation (Scheme 4) to either alcohols, ketones or aldehydes.\textsuperscript{100,101}

\[ \text{hv} \quad \text{R-H} \quad \text{O} \quad \text{Os VI} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{R-OH} \]

Scheme 4. Aerobic oxidation of saturated alkanes with metal-oxo complexes through irradiation

Selective photocatalytic conversion of cyclohexane into cyclohexanol with higher selectivity with molecular oxygen over quantum confined iron doped TiO\textsubscript{2} (Q-TiO\textsubscript{2}/Fe\textsuperscript{3+1}) nanoparticles\textsuperscript{102} under visible irradiation and mild conditions\textsuperscript{103,104} with the following mechanism (Scheme 5) should be considered as a mile stone.

\[
\text{TiO}_2 + \text{hv} \quad \rightarrow \quad \text{e}_{\text{CB}}^- + \text{h}_{\text{VB}}^+ \\
\text{Charge pair generation} \\
\text{Ti}^{4+} + \text{e}_{\text{CB}}^- \quad \rightarrow \quad \text{Ti}^{3+} \\
\text{Charge trapping} \\
\text{Bulk-Fe}^{3+} + \text{h}_{\text{VB}}^+ \quad \rightarrow \quad \text{Fe}^{3+} - \text{e}_{\text{CB}}^- \\
\text{Surf-Fe}^{3+} + \text{h}_{\text{VB}}^+ \quad \rightarrow \quad \text{Fe}^{3+} - \text{h}_{\text{VB}}^+ \\
\text{OH}^- + \text{h}_{\text{VB}}^+ \quad \rightarrow \quad \text{OH}^+ \\
\]
Charge release and migration

$$Fe^{3+} e_{CB}^{-} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}$$
$$Fe^{3+} h_{VB}^{+} + OH^{-} \rightarrow Fe^{3+} + Ti^{3+}$$

Interfacial charge transfer

$$e_{CB}^{-} (or Ti^{3+}, Fe^{3+} - e_{CB}^{-}) + O_2 \rightarrow O_2^{*-}$$
$$\text{H}_2\text{O}$$
$$\text{H}_2\text{O}_2 \rightarrow OH^{*}$$

$$h_{VB}^{+} (or OH^{*}, Fe^{3+} - h_{VB}^{+})$$

$$\text{Cyclohexane}^{*} + H^{+}$$

$$\text{Cyclohexane}^{*} + OH^{*} \rightarrow \text{Cyclohexane} - \text{H}_2\text{O}$$
$$\text{OH}^{*}$$
$$\text{CO}_2 + \text{H}_2\text{O}$$

**Scheme 5.** Selective oxidation of cyclohexane with oxygen over Q TiO$_2$/Fe$^{3+}$ nano particles

The reactions of coupling between the alkane oxidation and the nitrous compounds and a detailed chemical kinetic modelling investigations reproduces the temperature dependence of the conversion of the reactants and the species concentration profiles versus the residence time in the reactor.

### 4.8 Oxidation of branched paraffins

In general the free radical substitution is the expected reaction of saturated hydrocarbons. The reactivity of different C-H bonds vis-a-vis peroxy radicals is in the increasing order of primary C-H < secondary C-H < tertiary C-H bond. In the case of gas phase oxidation at 350°C, the relative reaction rates are in the ratio of 1:4:11. Even in liquid phase oxidation of the branched paraffins, the tertiary C-H bonds react preferably. Also in the
case of isobutane\textsuperscript{106,107} and isopentane\textsuperscript{108} (2-methylbutane) in liquid phase oxidation at 100-150°C the corresponding tertiary hydroperoxides were the first reaction products. Sutton and coworkers showed the relative velocity of a tertiary C-H bond to a primary C-H bond in the oxidation of 5-methyl nonane in the ratio of 50:01. Rust examined the liquid phase oxidation of a doubly branched alkane and concluded the formation of a bis-hydroperoxide\textsuperscript{37} even at lower turnovers. The intramolecular C-H cleavage is responsible for it. Such hydrogen transfers take place in considerable proportions only when the six membered transition states are possible and when the C-H bond undergoing the cleavage is a tertiary one. Rusts findings in the oxidation of 2,3-dimethylpantane and 2,6-dimethylheptane that no noticeable bis-hydroperoxide was formed by lower turnovers were confirmed by other authors\textsuperscript{109-111}. Higher simple branched paraffins gave higher yields of bifunctional oxidation products\textsuperscript{112,113} compared to the unbranched paraffins. It obviously points to the claim that those peroxo radicals whose peroxo groups are attached to the 3\textsuperscript{rd} or 4\textsuperscript{th} carbon atom to the tertiary C-H bond react through intramolecular H-transfer. The decomposition of the tertiary hydroperoxide under the conditions of hydrocarbon oxidation was studied in the case of tertiary-amyl hydroperoxide. The main reactions of the decompositions in the presence of isopentane as solvent are the fragmentation of tertiary alkoxy radicals,

\[
\begin{align*}
\text{CH}_3\text{-CH}_2\text{-C-O}^+ & \rightarrow \text{CH}_3\text{-CH}_2^+ + \text{CH}_3\text{-C-O} \\
\text{CH}_3\text{-CH}_2\text{-CH}_3 & \rightarrow \text{CH}_3\text{-CH}_2^+ + \text{CH}_3\text{-C-O}
\end{align*}
\]

and H-atom abstraction from the solvent

\[
\begin{align*}
\text{CH}_3\text{-CH}_2\text{-C-O}^+ + \text{R-H} & \rightarrow \text{CH}_3\text{-CH}_2\text{-C-OH} + \text{R}' \\
\text{CH}_3\text{-CH}_2\text{-CH}_3 & \rightarrow \text{CH}_3\text{-CH}_2\text{-C-OH} + \text{R}'
\end{align*}
\]
Ethanol and acetic acid which are the consecutive products of the ethyl radicals formed due to fragmentation are obtained as reaction products besides acetone and tertiary-amyl alcohol. The decomposition of tert-butylhydroperoxide in isobutene as solvent takes place in analogous. It is considered that the oxidation of branched paraffins takes place in analogue to the oxidation of normal branched paraffins. The oxidizabilities and reaction velocities of the elementary reactions of the oxidation of n-paraffins like isobutane\textsuperscript{115-117}, 2,3-dimethyl butane\textsuperscript{114}, 2,4-dimethylpentane and 2,4,6-trimethylheptane were published. The oxidizability of n-paraffins increases as expected with increase in chain length. The chain termination velocities do not differ substantially. The chain propagation velocities\textsuperscript{118} increase with the increase in the chain length. It is not more in isoparaffins than the n-paraffins. It is dependent upon together with that in the isoparaffins compared to the n-paraffins not only a specially active tertiary C-H bond but also three extra primary C-H bonds are present. By the transition of a n-paraffin to isomeric isoparaffin four secondary C-H bonds disappear while a tertiary and three C-H bonds newly form.

4.9 Thermal oxidation of 1-phenylheptane

100 mmol of 1-phenylheptane analyzed by gas chromatography was subjected to autoxidation in an open oxidation apparatus for about 60 hours at \(\sim\)100\(^\circ\)C with 5 L/h \(\text{O}_2\) in chloro benzene as solvent. The oxidation mixture after concentration was subjected to GC and GC/MS analysis. The GC pattern of the oxidate is given in the fig.1. The GC/MS and MS spectra are given in fig. 2 and 3-14 respectively.
Table 1: Chromatographic investigation of the products of the oxidation of 1-phenylheptane

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<th>Height</th>
<th>Conc.</th>
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<td>Area (%)</td>
<td>Compound$^a$</td>
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<td>1-phenyl-heptan-1-ol</td>
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</table>

a) Identification has been done from both GC and GC/MS methods.

The concentration parameters have been taken from the gas chromatographic analysis. The percentage of the identified products has been calculated on the basis of the converted portion of the starting hydrocarbon. The components have been identified from mass spectrum of the GC/MS recording. The identification is based both on the fragmentation pattern and the comparison of the mass spectrum with the authentic ones.
Spectrum Plot

File: C:\GCQ\DATA\589
Date: Jan-30-2006 15:15:35

Comment: Sample-1 from (GLT) on Innowax cap E1+
Scan No: 2779 Retention Time: 46:23 RIC: 7496392 Mass Range: 30 - 348
# Peaks: 276 Base Pk: 107 Ioniz: 299 us Int: 2368099 100.00% = 2368099

100 % 107

INT

39 51 65 91 115 131 155 175 192

Fig. 14
Spectrum Plot
File: C:\GCQ\DATA\589  Date: Jan-30-2006  15:15:35
Comment: Sample-1 from (GLT) on Innowax cap    EI+
Scan No: 910  Retention Time: 15:13  RIC: 1318895  Mass Range: 30 - 348
# Peaks: 254  Base Pk: 91  Ioniz: 1259 us  Int: 521710  100.00% = 521710

100 %

INT

134

65

39 51 77 105 115 147 183 199 225 262 279 295 310 343

20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360

Fig. 5
Spectrum Plot

File: \GCQ\DATA\589
Date: Jan - 30 - 2006 15:15:35

Comment: Sample-1 from (GLT) on Innowax cap EI+
# Peaks: 268 Base Pk: 105 Ioniz: 1097 us Int: 557237 100.00% - 557237

100 %

INT

105

77

51

63 95 128 155 183 233 262 278 298 329 344

20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360

Date: May 20th, 2006 3:51pm GCQ Data Processing, Finnigan Corporation

Fig. 8
Spectrum Plot

File: C:\GCQ\DATA\589
Date: Jan - 30 - 2006 15:15:35

Comment: Sample-1 from (GLT) on Innowax cap EI+
Scan No: 1714 Retention Time: 28.37 RIC: 818155 Mass Range: 31 - 349
# Peaks: 290 Base Pk: 91 Ioniz: 1997 ms Int: 226198 100.00% = 226198

Fig. 11
Spectrum Plot

File: C:\GCQ\DATA\589
Date: Jan - 30 - 2006 15:15:35

Comment: Sample-1 from (GLT) on Innowax cap EI+
Scan No: 2413 Retention Time: 40:16 RIC: 28626170 Mass Range: 31 - 349
# Peaks: 280 Base Pk: 105 Ioniz: 119 us Int: 6895472 100:00% = 6895472

100%  

INT

105

120

190

51  77

91  133

147

209  240  267  294  322  339

20  40  60  80  100  120  140  160  180  200  220  240  260  280  300  320  340  360

Date: May 20th, 2006 4:02pm GCQ Data Processing, Finnigan Corporation

Fig. 13
The pattern of the components has been the same in gas chromatogram and the GC of the GC/MS. The retention times are taken from the GC/MS spectrum.

Under the experimental conditions, the formation of 1-phenyl-heptan-1-ol and 1-phenyl-1-heptanone as major oxidation products is considered as the decomposition products of the corresponding hydroperoxide which resulted due to the oxidative attack at the benzylic position. The percentage composition of 1-phenyl-1-heptanone is about three times more than that of 1-phenyl-heptan-1-ol. This is due to the fact that the rate of oxidation of the said alcohol to the ketone is several times faster. The formation of 1-phenylheptan-3-one and 1-phenylheptan-5-one although in minor quantities indicates the C-H bond activation at 3 and 5 positions with respect to the phenyl ring. This leads to the conclusion that the substitution of phenyl group in n-octane (at the terminal position) suppresses the oxidative attack of the methylene groups present at different positions other than the benzylic one. The formation of 1-phenyl-1-propanone and 3-phenylpropanal should be considered due to the C-C bond cleavage of the side chain.
References


100. Yan, V.W.W., Che, C.M., Coord. Chem. Rev., 1990, 97, 93.


