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Review Article

Oxidation of Alkylaromatics

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Abstract: Hydroperoxide at α -position to the aromatic ring is the primary oxidation product formed. In all cases monoalkylbenzenes lead to the formation of benzoic acid. Oxidation in the presence of transition metal salts not only accelerate but also selectively decompose the hydroperoxides. Alkyl naphthalenes mainly produce the corresponding naphthalene carboxylic acids. Hock-rearrangement by the influence of strong acids converts the hydroperoxides to hemiacetals. Peresters formed from the hydroperoxides undergo Criegee rearrangement easily. Alkali metals accelerate the oxidation while CO_2 as co-oxidant enhances the selectivity. Microwave conditions give improved yields of the oxidation products.

Keywords: α -hydroperoxides, carboxylic acids, alkylbenzenes, alkyl-naphthalenes, Hock-rearrangement, Criegee-rearrangement.

Introduction

The first examination of alkylaromatics with molecular oxygen was published by Ciamician and Silber¹. The authors allowed toluene, *o*-xylene, *m*-xylene, *p*-xylene and *p*-cymene for about a year to be influenced by oxygen and sunlight. The corresponding monocarboxylic acids were obtained as main products. Iso and terephthalic acids were formed besides *m*- and *p*-toluyl acids from *m*- and *p*-xylenes respectively. Stephens²⁻⁶ engaged with the oxidation of *m*-xylene, mesitylene, durene and *p*-cymene obtained the corresponding benzaldehyde derivatives² in small amounts after interacting with molecular oxygen at the temperatures of $\sim 100^\circ\text{C}$. Under these conditions, acetophenone³ and propiophenone³ were obtained from ethylbenzene and *n*-propylbenzene respectively. Cumene³, 2-phenylbutane⁶, 2-phenylpentane⁶ and 2-phenylhexane⁶ also gave acetophenone on oxidation. Diphenylmethane⁶ and 1,1-diphenylethane⁶ were oxidized to benzophenone. Hartmann and Seiberth isolated for the first time a hydroperoxide⁷ while others engaged in oxidation of

alkylaromatics could only find the consecutive products of the oxidation. Hartmann and later Hock and Susemihl⁸ succeeded independently in the isolation of crystalline peroxide in the oxidation of tetralin at 70-80°C and identified it as α -hydroperoxy tetralin. Hock and Lang showed that in the oxidation of indane⁹ and from simple alkylaromatics like *p*-xylene¹⁰, ethylbenzene¹⁰ and cumene¹¹, the corresponding hydroperoxides as primary products could be isolated in which the -OOH group is present at the carbon atom at α -position to the aromatic ring. IG-Farben processed a method for the oxidation of ethylbenzene¹². The oxidation carried out continuously at 120-130°C in the presence of Mn-acetate gave a mixture of acetophenone and phenylmethyl carbinol which was further processed to styrene. This method is not technically beneficial as styrene can be obtained directly from ethylbenzene by dehydrogenation¹³.

IG-Farben realized the oxidation of toluene to benzoic acid very easily at 130-150°C/0.3-0.5MPa in the presence of Co-salts. It was later shown that better yields¹⁴ of benzoic acid could be obtained by the oxidation of toluene and other monoalkylbenzenes in glacial acetic acid as solvent. Oxidation of Toluene over V₂O₅-Sb₂O₃/TiO₂ catalysts in the presence of carbon-dioxide showed an enhancement of selectivity¹⁵ to benzoic acid formation. The promotional effect of CO₂ in the liquid phase oxidation of ethylbenzene with molecular oxygen to acetophenone with Co/Mn/Br (MC-type) catalyst system could be demonstrated by the enhancement of the catalytic activity and thus selectivity towards acetophenone¹⁶ and suppression of side reactions. In the course of oxidations over transition metal/CO₂ catalyst systems, a metal (Co or Mn, MC-type catalyst system) peroxy-carbonate complex^{17,18} has been proposed as the catalytically active species responsible for the oxidative transformation of alkyl aromatic substrates, in the presence of CO₂. The formation of this complex has been proposed to occur in two stages:

1. Formation of an MO₂ oxo-moiety and
2. Cleavage of the M-O bond and the simultaneous insertion of CO₂ to form the metal peroxy-carbonate complex which is catalytically reactive and mediates the oxidation of alkyl aromatics.

The findings of Hock and Lang lead to the technical method of cumene-phenol processing by the decomposition of cumene hydroperoxide to phenol and acetone through strong acids. Oxidation of cumene was later carried out in aqueous-alkaline emulsion at 80-140°C and later by homogenous oxidation^{19,20} at 120-130°C.

Two processes to oxidize *p*-xylene to produce dimethyl terephthalate or terephthalic acid were developed. The direct oxidation of *p*-xylene to terephthalic acid is very difficult and as the *p*-toluyl acid formed as intermediate is very heavy, terephthalic acid is almost not soluble. Therefore, Katzschmann recommended to carryout the oxidation in two steps. In the first step *p*-toluyl acid is produced and in the second, the methyl ester of *p*-toluyl acid is converted to terephthalic acid monomethyl ester. The one step oxidation of *p*-xylene to terephthalic acid at 170-230°C/0.5-2.0 MPa²¹ was carried out besides the catalytic systems from transition metal ions and bromide ions. In the same way, isophthalic acid was also produced from *m*-xylene²².

The oxidation studies of *p*-xylene showed 4-carboxybenzaldehyde²³ as an unstable intermediate and the reaction proceeded instantaneously from *p*-toluic acid to TPA. The alkali metals²⁴ accelerates the oxidation while CO₂ as a co-oxidant²⁵ also promotes the reaction.

A new heterogeneous catalyst based on a chemically modified mesoporous silica gel supported Schiff base complex²⁶ was successfully applied to the aerial oxidation of alkyl aromatics at atmospheric pressure and in the absence of solvent.

The studies of the shape selectivity in the liquid-phase hydroxylation²⁷ of aromatic hydrocarbons with hydrogen peroxide on the large-pore Ti-M with MOR structure and medium-pore TS-1 with MFI structure conclude that a bulky Ti-peroxo species (Ti-OOH) formed by the interaction of Ti site with H₂O₂ mainly causes a transition-state shape selectivity in the hydroxylation of bulky aromatics in titanosilicate/H₂O₂ systems (Figure 1).

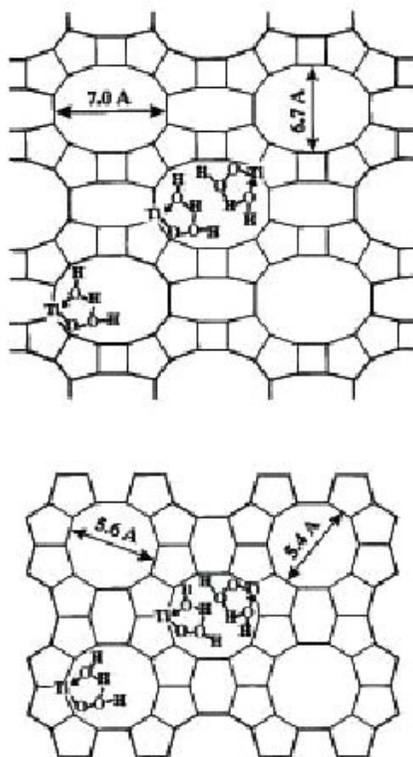


Figure 1.

The observation of 4-hydroxy-4-methyl-2,5-cyclohexadiene 1-one as a product in the radiolysis of aqueous solution is important in demonstrating that addition of $\cdot\text{OH}$ radicals to aromatic rings at positions substituted with alkyl groups can be of appreciable importance in the $\cdot\text{OH}$ oxidation²⁸ of aromatic substrate.

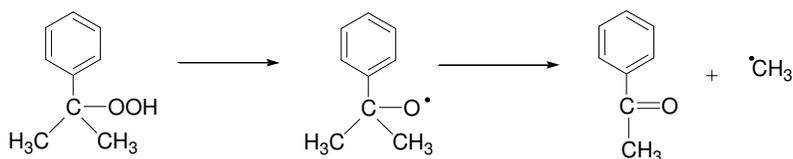
Oxidation of monoalkylbenzene

Toluene and ethylbenzene undergo oxidation with considerable velocities at $\sim 120^\circ\text{C}$ in the absence of initiators. The primary products are the corresponding hydroperoxides which are not obtained in higher amounts due to their instability²⁹⁻³¹. The maximum obtainable hydroperoxide concentration would be determined through that concentration by which the rate of formation and the decomposition are almost equal. The hydroperoxide from cumene and sec-butylbenzene form easily and relatively more stable. Cumene hydroperoxide is

technically important which serves as the intermediate product for the synthesis of phenol^{32,33} and of α -methyl styrene³⁴. Cumene hydroperoxide and sec-butylbenzene hydroperoxide can be produced either through oxidation of the hydrocarbons in aqueous alkaline emulsion²⁰ at 85-120°C or through oxidation in the absence of aqueous medium preferably by the addition of alkalis like NaOH or Na₂CO₃. The accelerated influence by alkali additions in the oxidation of cumene on one side comes to a state where the organic acids formed by side reactions and consecutive reactions (preferably formic acid) would be neutralized through which the acid cleavage of the hydroperoxide to phenol and acetone be checked and on the other side the alkalis cause radical decomposition of the cumene hydroperoxide and through that an increase in the initiation velocity. The radical decomposition of hydroperoxides through alkalis and the catalytic effect of alkali hydroxides and carbonates in cumene oxidation can be suppressed when carried out in the presence of small quantities of ethylenediaminetetraacetic acid³⁵. It is probably due to catalysis through traces of heavy metal salts where the base acts only as a co-catalyst.

The excess of addition of transition metal compounds in the oxidation of cumene should not be preferable although references are available for the high increase of the velocities⁴ of the cumene oxidation reactions by the addition of metallic copper³⁶, Cu-phthalocyanin^{37,38} and lead oxide³⁹ as the selectivity of the hydroperoxide formation is considerably lowered. One obtains the decomposition products of the primarily formed hydroperoxides under the favorable conditions for e.g. in the presence of strongly effecting catalysts like Co- or Mn-compounds. By higher temperatures or by higher turnovers, the decomposition products of the hydroperoxides and their further consecutive products dominate. The radical decomposition of benzyl hydroperoxide leads to benzaldehyde and benzyl alcohol⁴⁰ while ethylbenzene hydroperoxide delivers 1-phenylethanol⁴¹ and acetophenone. In the radical decomposition of cumene hydroperoxide, one finds to a considerable extent, the fragmentation of the cumyloxy radicals formed as intermediate finally forming acetophenone, methane, ethane and methanol⁴²⁻⁴⁵. The fragmentation share increases with the increase in temperature. One obtains from cumene hydroperoxide in cumene as solvent below the temperatures of 100°C preferably 2-phenylpropan-2-ol while acetophenone formation is favoured at 150°C (Scheme 1).

The radical decomposition of sec-butylbenzene hydroperoxide takes place in an analogue to the cumene hydroperoxide leading to the formation of 2-phenylbutan-2-ol and acetophenone. An ethyl group is preferably cleaved off. Further oxidation of the decomposition products of the hydroperoxide leads to benzoic acid at the end in all cases. The further oxidation is favoured⁴⁶ when it is carried out at temperatures of 150°C in butanoic acid as solvent. It must be established that in the case of ethylbenzene, the further oxidation of acetophenone takes place very slowly compared to the oxidation of the starting hydrocarbon so that higher yields of acetophenone can be obtained^{47,48}. As like in the case of other tertiary alcohols, the mechanism of the further oxidation of 2-phenylpropane-2-ol is exactly not known. The oxidation takes place surely via acetophenone⁴⁹ and proceeds at the end to benzoic acid. It is also possible that the reaction takes place via dehydration and then the further oxidation of the α -methylstyrene formed. Benzoic acid is obtained as expected when the oxidation is carried out in acetic acid as solvent and in the presence of bromide containing catalyst systems from toluene, ethylbenzene and cumene. The further oxidation of the acetophenone formed from ethylbenzene and cumene respectively creates difficulties in the oxidations.

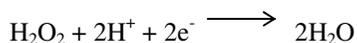


Scheme 1

The alkylbenzenes especially ethylbenzene and cumene undergo oxidation easily and therefore the transition of oxygen from gas phase in the liquid phase of the oxidized hydrocarbon is often the velocity determining step of the oxidation. Therefore, the rate of oxidation is dependent upon the partial pressure of oxygen. The oxidates from cumene and ethylbenzene contain dimerisation products of the hydrocarbon radical.

Tertiary butylbenzene doesn't contain C-H bond at α -position to the benzene and therefore the conditions are also not suitable in this case for the formation of a hydrocarbon free radical which can be stabilized by mesomerism. Due to this, tert-butylbenzene would not be attacked under the conditions of the oxidation of toluene, ethylbenzene, cumene and secondary butylbenzene. The phenylcycloalkanes can be denoted not only as alkylbenzenes but also as substitution products of cycloalkanes. Phenyl cyclopentane possesses the highest oxidizability among the comparable phenylcycloalkanes. If the turnover is kept lower than 20%, one can obtain the hydroperoxide yields⁵⁰ from 92 to 95% of the tertiary isomer and ~10% of the secondary isomer. By increasing the turnovers, the decomposition products of tertiary hydroperoxide (phenyl-n-butylketone) and the secondary hydroperoxide (phenylcyclopentane) are formed. The expected alcohol (phenylcyclopentanol) was not found in the reaction mixture.

Hydrogen peroxide except oxygen is unique in that, its only byproduct is water. It has the highest percent of active oxygen⁵¹ and therefore the generation of effluents is lower. It is a highly pure, very stable (over a range of conditions) and can be used in both aqueous and organic media. It is a powerful oxidant ($E^\circ = 1.76V$)

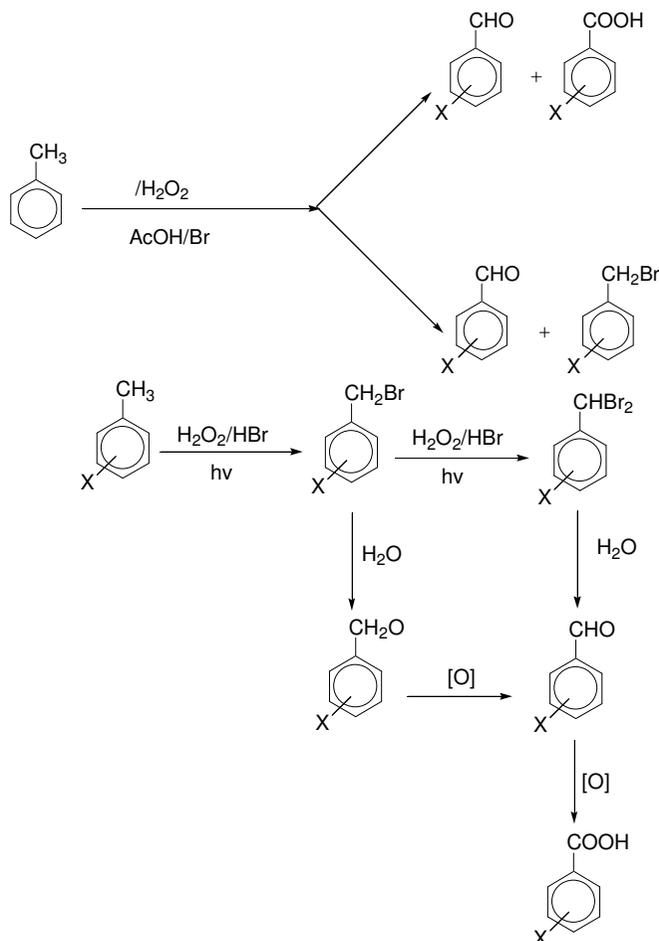


It's peroxide functionality can be activated⁵² by transition metal ions or also occur by interaction of H_2O_2 with an organic compound.

The alkyl side chains of aromatic rings can undergo oxidation by several mechanisms. The most common mechanism is the direct attack by the oxidation at benzylic carbon as the intermediate formed is stabilized by the resonance structure of the ring. The resonance stabilization doesn't arise when the oxidant attacks another atom in the alkyl side chain. The product selectivity can be controlled towards aldehyde⁵³. Aromatic side chains can be oxidized directly to the desired compounds by peroxygen or via halogenation. The oxidation of benzylic positions to carbonyl group is one of the most important transformations in synthetic chemistry⁵⁴. Alkyl-substituted benzenes with *o*-cholranil gave 1,3-benzodioxoles via benzylic oxidation and subsequent acetal formation⁵⁵ was shown.



Solvay Interlox technology⁵⁶ for side chain oxidation can be represented as (Scheme 2).



Active transition metal species (Co, Cu, Cr, Ni, or Mn) supported on the modified silica gel promotes the oxidation of aromatic side chains⁵⁷ using either air or molecular oxygen as the oxidant rather than peroxides or peracids.

Oxidation of di and polyalkylbenzenes

The oxidation of the isomeric xylenes is possible around 120°C and has high technical importance. The corresponding hydroperoxides were isolated when the oxidations were carried out in the absence of a catalyst^{58,59}. The hydroperoxides reach a maximum of 2% only and possess no technical importance. During the further oxidation, especially in the presence of Co or Mn salts, the hydroperoxides decompose to the corresponding toluyl alcohols and toluyl aldehydes which in turn are oxidized easily to toluyl acids. The toluyl acids are very difficult to be oxidized to the corresponding benzene dicarboxylic acids. They can be obtained from xylenes in good yields. The oxidation of xylenes in acetic acid as solvent and in the presence of bromine containing catalyst systems e.g. CoBr₂ and or MnBr₂ leads to the corresponding benzene dicarboxylic acids in a one step reaction. By this method, terephthalic acid is obtained from *p*-xylene.

The oxidation of *m*- and *p*-diisopropylbenzene is also having technical importance. By careful oxidation, one obtains a mixture of mono and dihydroperoxides⁶⁰ from which the dihydroperoxide can be isolated by treating the mixture with 5-10% NaOH. The *p*-diisopropylbenzene dihydroperoxide with strong acids decomposes to hydroquinone and acetone. Iso or terephthalic acids⁶¹ are obtained in good yields when *m*-and/or *p*-diisopropylbenzene is oxidized in lower carboxylic acids (mainly in acetic acid or propanoic acid) in the presence of Co and/or Co salts at 120-150°C and 0.2 to 0.8 MPa. The rate of reaction can be increased by using bromide containing catalyst systems. The tertiary alcohols and acetophenone derivatives formed by the radical decomposition of the hydroperoxides could be further oxidized to the corresponding benzene carboxylic acids.

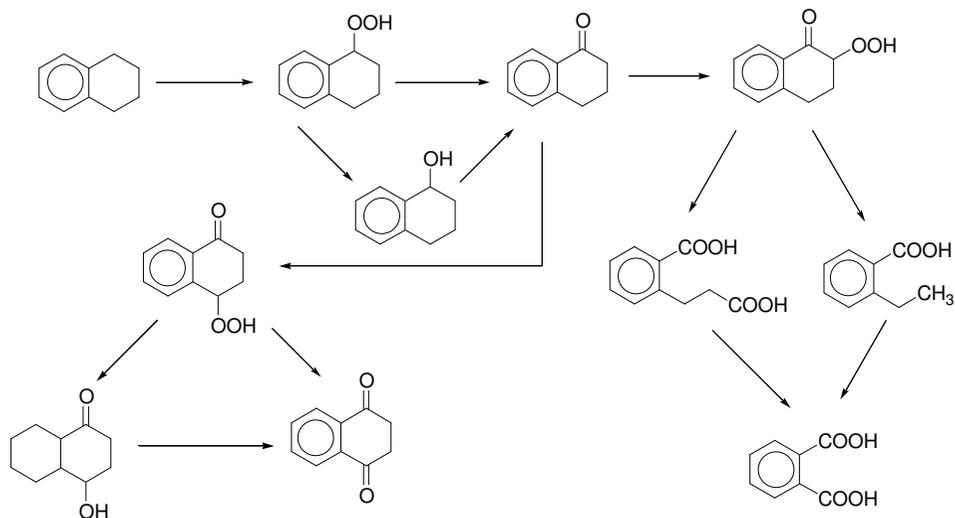
Oxidation of *p*-ethyl toluene in the presence of transition metal salts gives *p*-methyl acetophenone as the main product (~32%) and ethyl benzoic acid (~10%)⁶². From the results, it was concluded that a secondary C-H bond was 5 times easily attacked than a primary C-H bond. Several authors showed that the isopropyl group is attacked in preference to the methyl group in the oxidation of *p*-cymene⁶³⁻⁶⁶ leading to the formation of a hydroperoxide mixture containing 86% of tertiary and 14% of primary isomers⁶⁷. It was shown that rate of tertiary C-H bond is 18 times more than a primary C-H bond.

The tertiary butyltoluene contains an activated C-H bond only in the methyl group and therefore delivers *p*-tert-butyl benzoic acid as tert-butyl group would not be attacked. Mesitylene, pseudocumene and 1,3,5-triisopropyl benzene the important trialkylbenzenes were oxidized to the corresponding benzene tricarboxylic acids in acetic acid with bromide containing catalyst systems e.g. CoBr₂ and or MnBr₂. Under tetraalkyl benzenes, the most important one is durene. One can obtain pyromellith acid, 5-methyltrimellith acid or durene acid.

Oxidation of alkyl naphthalenes

α - and β -methyl naphthalenes are oxidized in acetic acid as solvent in the presence of catalyst systems like the transition metal ions (Co²⁺ and Mn²⁺) and bromide ion containing ones to the corresponding naphthalene carboxylic acids at > 120°C and 1 to 2 MPa. The reported yields are ~80%. In a similar way, one can oxidize the dimethyl naphthalene e.g. 2,6-dimethyl naphthalene to the corresponding naphthalene dicarboxylic acid. Amongst the two isopropyl naphthalenes, only β -isomer is oxidized to the corresponding hydroperoxide at 100°C easily. The α -isomer would not be oxidized under these conditions, as in the corresponding carbon free radical, a planar position of the substituents is not possible⁶⁸. When the isomer mixture of isopropyl naphthalenes is employed, β -isopropyl naphthalene hydroperoxide, is also obtained accordingly. From this hydroperoxide one can produce β -naphthol through acid decomposition. Indane and tetralin are easily oxidisable and deliver high yields of the corresponding α -hydroperoxides. Robertson concluded from the oxidation of tetralin⁶⁹⁻⁷² at 70 - 80°C that in the first phase of the reaction, the hydroperoxide formed decomposes to α -tetralone and to α -tetralol in the second phase while in the third phase the decomposition products were further oxidized. The important products of the further oxidation were β -(*o*-carboxyphenol) propanoic acid, γ -(*o*-hydroxyphenyl) butyraldehyde and γ -(*o*-hydroxy phenyl) butanoic acid. The two phenolic derivatives are responsible for the significant decrease in the reaction velocities at high turnovers. Their formation leads to the inhibition of the oxidation which was also observed in the case of alkylaromatics. The important products found were benzoic acid, *o*-ethylbenzoic acid, phthalic acid, tetralin-1-ol-4-one and tetralin-1,4-dione.

Trieb and coworkers examined the oxidation of some partially hydrogenated polyring aromatics and isolated the corresponding hydroperoxides⁷³⁻⁷⁷.



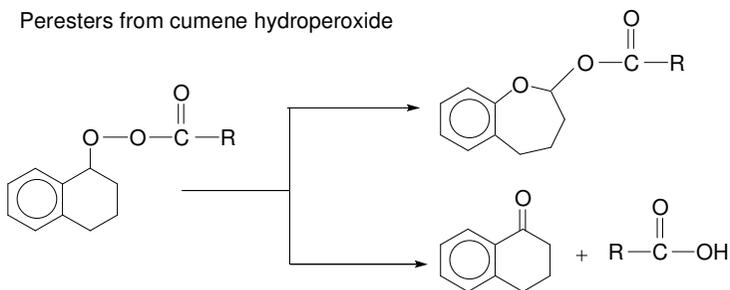
Scheme 3.

Oxidation of alkylaromatics under the conditions of Hock or the Criegee-rearrangement

Hydroperoxides by the reaction with acylation agents gave the corresponding peresters which undergo Criegee-rearrangement^{78,79} easily.



Peresters from cumene hydroperoxide

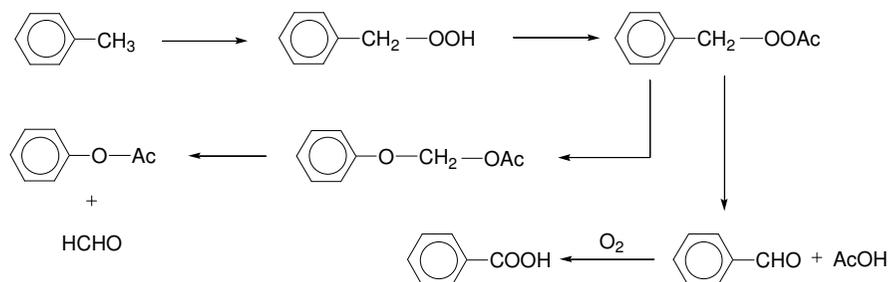


Perester from tetralin hydroperoxide

Scheme 4.

Hydroperoxides undergo Hock-rearrangement by the influence of strong acids to hemiacetals.

One should expect the formation of peracetate of the corresponding hydroperoxide and its Criegee-rearrangement product in the oxidation of alkylaromatics carried out in the presence of acetic anhydride. The principle was applied by Shine and Synder in the oxidation of tetralin. As expected, α -tetralone and the product of Criegee-rearrangement of α -tetralyl peracetate were obtained. It was concluded that for better reaction velocities, one has to work at high temperatures and pressures and the reaction mixture of the starting hydrocarbon and acetic anhydride should not be treated with sulphuric acid in parts.



Scheme 7.

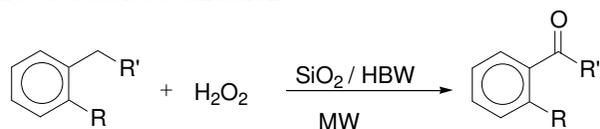
Kinetics of alkylaromatics

After saponification, the yields of the phenols e.g. phenol from toluene, *p*-cresol from *p*-xylene etc. amounted to 50%. From this, one could even conclude to obtain pure cresol from the isomeric xylenes. The oxidisabilities $\left(k_p / \sqrt{2k_t}\right)$ of alkylaromatics were first published by Russell⁸³. The values for k_t and k_p along with oxidisabilities for a large number of alkylaromatics⁸⁴ at 30° were examined by Howard and Ingold. The authors also determined the velocity constants for different turnovers of alkyl benzenes with cumyl peroxy radicals⁸⁵. The velocity constants for the reaction of hydrocarbons with cumyl peroxy radicals are generally lower than the corresponding values for the reaction of hydrocarbons with their own peroxy radicals⁸⁵. Pritzkow and Rosner⁸⁶ determined relative values for chain propagation velocities in the autoxidation of a large number of alkyl aromatics.

Photo-oxidation

Photo-oxidation products⁸⁷ from the reaction of a series of alkyl-benzenes (benzene, toluene, *p*-xylene and 1,3,5-trimethylbenzene) with hydroxyl radicals in the presence of NO_x showed the presence of maleic anhydride, citraconic anhydride, benzaldehyde and *p*-methyl benzoquinone in toluene reactions, *E/Z*-hex-3-en-2,5-dione and citraconic anhydride in *p*-xylene experiment while 1,3,5-TMB reactions showed the presence of 3,5-dimethylbenzaldehyde, 3,5-dimethyl-3H-furan-2-one and 3-methyl-5-methylene-5H-furan-2-one. Toluene photooxidation⁸⁸ is chosen as an example to examine how simulations of smog-chamber experiments can be used to unravel shortcomings in detailed mechanisms and to provide information on complex systems that will be crucial to the design of the future validation experiments. The evaluation of MCMv 3 and MCMv 3.1 using data on benzene, toluene, *p*-xylene and 1,3,5-trimethylbenzene photo smog systems and details of aromatic photooxidation⁸⁹ were discussed. The radical budget has been examined in detail through MCM simulations, which shows that the major route⁹⁰ contributing to radical formation is that involving opening of the aromatic ring and formation of dicarbonyl intermediates. Potential sources of radicals are suggested, including decomposition of peroxy radicals and heterogeneous reactions of NO_2 .

There is still the growing interest in novel methods which will not suffer from toxic wastes and can be characterized by high yield and selectivity. The oxidation by H_2O_2 ^{91,92} at microwave conditions⁹³, some arenes with the alkyl side groups as the substrate were shown susceptible to microwave assisted oxidation.



Scheme 8.

It was observed that microwave irradiation improves the oxidation and the yields were higher than those from conventional experiments⁹⁴. Heterogeneous reactions were characterized by higher effectiveness than homogeneous reactions.

Conclusions

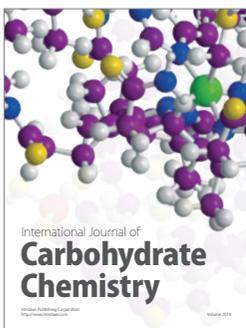
The alkyl side chain of aromatic rings can undergo oxidation by several mechanisms. The most common and dominant one is the attack by oxidation at benzylic carbon as the intermediate formed is stabilized by resonance structure of the ring. To add to the industrial processes like the production of phenol and acetone from cumene and terephthalic acid from p-xylene, one has to work with photo smog systems and micro-wave conditions. Better yields of some desired products may be obtained if some of the products formed can be removed during oxidation.

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