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The Montmorillonite Catalysed Conversion of Hydroperoxides

W.A. de Groot
THE MONTMORILLONITE CATALYSED
CONVERSION OF HYDROPEROXIDES

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SUMMARY

Many food products contain fats and oils, and in the last decades a shift towards the use of vegetable oils with high contents of (poly-)unsaturated fatty acids is observed. This is related to the positive properties of these fatty acids, in reducing the risk of coronary heart diseases. A disadvantage of unsaturated fatty acids however is their susceptibility towards oxidation, resulting in the formation of hydroperoxides as primary products. Hydroperoxides are relatively unstable components, which during decomposition give rise to the formation of powerful flavour components, contributing to the rancidity of the food product. Crude oils with high contents of poly-unsaturated fatty acids inevitably contain certain amounts of hydroperoxides, which are being converted during refining by treatment with a bleaching earth. A bleaching earth is an acid-activated clay mineral of the montmorillonite type. The insight in the chemical processes occurring during bleaching is rather limited. By studying the conversion of hydroperoxides as a function of several process conditions, it was attempted to increase this limited insight.

A literature overview has been given of the chemistry of fatty acid hydroperoxides. These are formed via an autocatalytic oxidation process. When fatty acid hydroperoxides are subjected to higher temperatures, radical reactions are initiated, leading to a complex product mixture varying from cleavage products, which generally are the flavour components, via fatty acid products with different functionalities to oligomeric material. Knowledge about the acid catalysed decomposition, as expected to occur during bleaching, is limited. Cleavage according to the Hock mechanism, a general reaction for hydroperoxides linked to a conjugated system, as well as the formation of polyhydroxy components is reported.

For the experimental investigations one fatty acid hydroperoxide has been used: 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid (13-c,t-HPOD), which has been
produced enzymatically. This hydroperoxide isomer is one of the four hydroperoxide isomers being formed during oxidation of linoleic acid. This approach minimises the complexity of the product mixture. By studying the hydroperoxide in its free fatty acid form, the analysis of the reaction mixture is furthermore facilitated. As solvent an inert triglyceride, MCT-oil, which has the physical properties of a vegetable oil, was chosen. Next to the fatty acid hydroperoxide, cumene hydroperoxide (CHP) has also been used. Cumene hydroperoxide can be considered as a model for polyunsaturated fatty acids, because of analogies in the molecular structure, based on which analogue reactions are expected. Analysis of the latter system is much easier and since no catalyst deactivation occurs, a detailed kinetic study could be performed. This process is furthermore interesting from an industrial point of view, because phenol and acetone are being produced.

The conversions of the hydroperoxides have been carried out batch wise with different commercial montmorillonite catalysts, varying in acid strength as a consequence of different degrees of acid-activation. The temperature has been varied between 273 - 323 K (CHP) or 323 - 413 K (13-c,t-HPOD), with initial hydroperoxide concentrations up to 500 mol m\(^{-3}\) (CHP) or up to 60 mol m\(^{-3}\) (13-c,t-HPOD) and montmorillonite concentrations up to 1 kg m\(^{-3}\) (CHP) or up to 10 kg m\(^{-3}\) (13-c,t-HPOD). The water concentration has been varied from 2 - 300 mol m\(^{-3}\) (CHP) or from 15 - 120 mol m\(^{-3}\) (13-c,t-HPOD) and in addition the solvent has been varied. Catalysts have been characterised by elemental analysis and N\(_2\)-physisorption to determine the degree of deactivation.

CHP decomposes with a selectivity of 100% towards phenol and acetone at 100% conversion, with Filtrol F-20 as catalyst, and with a rate comparable to the current industrial process with sulphuric acid as catalyst. The Hock mechanism is responsible for this reaction. Water appears to strongly inhibit the catalytic activity. During the decomposition a new side-product, a hydroperoxide ketal of acetone, is formed with selectivities of up to 25%, which influences the rate of decomposition due to the simultaneous formation of water. Decomposition of the ketal also proceeds by the Hock mechanism. 2-phenyl-2-propanol, which is present for ± 5% in industrial CHP feed, inhibits the main reaction by the formation of water via a condensation reaction of 2-phenyl-2-propanol with CHP and by competitive adsorption. Catalysts with a lower acid strength, such as ACC FF and XJ-9126, are unable to convert cumene hydroperoxide under the conditions employed. A model, based on Langmuir-Hinshelwood kinetics, has been developed in order to quantitatively describe the observed reaction network in the temperature range of 283 -313 K with F-20 as catalyst. The model consists of 7 adsorption equilibria and 7 other reaction steps, of which some are reversible. The inhibiting effect of water has been incorporated via a partial negative reaction order for water in the acid catalysed reaction steps. Regression of the model with the experimental data by a multi-response Marquardt algorithm resulted in a set of 20 significantly estimated and
physically reasonable parameters, which can be used for industrial design purposes. The activation energy of the main reaction amounts to 105 kJ mol\(^{-1}\), while a strongly negative partial reaction order for water of -2.44 has been determined in the acid catalysed steps, corresponding to the strong sensitivity of clay catalysts for the water concentration.

The conversion of 13-c,t-HPOD is much more complex. With techniques, such as GC-MS, HPLC-MS and HPLC-UV, 16 non-volatile and 21 volatile components have been identified and quantified. The non-volatile components are the 13- and 9- and cis,trans- and trans,trans-isomers of hydroperoxy-, hydroxy- and oxo-octadecadienoic acid, in addition to octadecatrienoic acid, 12-oxo-10-trans-dodecenoic acid and the cis,trans- and trans,trans-isomers of 13-oxo-9,11-tridecadienoic acid. The volatile components mainly consist of (unsaturated) aldehydes, of which hexanal and decadienal are the most important. Quantification of these components results in product carbon balances which are closing for up to 38% during thermal conversion and up to 75% during the montmorillonite catalysed conversion.

The main products during the thermally induced conversion of 13-c,t-HPOD are the cleavage products hexanal and oxotridecadienoic acid, followed by oxo- and hydroxy-octadecadienoic acid respectively. Hexanal and oxotridecadienoic acid arise from cleavage of the \(C_{18}\)-chain at the different sides of the alkoxy radical derived from the corresponding hydroperoxide, while disproportionation with retention of the original stereoisomeric configuration is an acceptable mechanism for the oxo- and hydroxy-components. The polyunsaturated components are subject to consecutive reactions, most probably polymerisation reactions. The apparent activation energy for the thermally induced conversion amounts to 91 kJ mol\(^{-1}\), while the influence of the temperature on the selectivity is most pronounced for the cleavage products.

During the Supreme FF catalysed conversion of 13-c,t-HPOD, which at a temperature of 363 K takes place at a time scale of several ks, products which can be attributed to acid catalysed mechanisms are predominantly formed. The main products are hexanal and 12-oxo-10-trans-dodecenoic acid, which are formed by the Hock mechanism, followed by oxooctadecadienoic acid isomers as a result of a net dehydration and octadecatrienoic acid. Furthermore products, originating from thermally induced mechanisms, such as decadienal and oxotridecadienoic acid are formed. The most remarkable aspect of the network of the montmorillonite catalysed conversion, however, is that of the products formed ± 80% is formed via intermediates, for which dimeric components with a peroxide linkage are proposed. These intermediates are converted slower than 13-c,t-HPOD, but yield the same final products.

The conversion of 13-c,t-HPOD is influenced by the montmorillonite type, and the higher the acid strength, the faster the conversion. Furthermore, more of the
identified products are observed with the stronger acidic types, which leads to the conclusion that the weaker acidic types are less able to convert the intermediates. In contrast to the general trend for clay catalysed reactions, the water concentration does not show a visible effect on the conversion. The Hock mechanism becomes more important at lower water concentrations, whereas more oxooctadecadienoic acid is formed at higher water concentrations. More polar solvents furthermore appear to inhibit the conversion to some degree.

An important phenomenon is the extreme deactivation of the montmorillonite catalysts during the conversion of 13-c,t-HPOD. After a reaction time of 3 ks at 363 K in MCT-oil, in which the 13-c,t-HPOD with an initial concentration of 30 mol m$^{-3}$ has been converted completely, the degree of deactivation amounts to 90%. The deactivation appears to proceed via the process of parallel deactivation, and material probably resulting from polymerisation reactions at the surface is irreversibly deposited, resulting in pore blockage and a decrease of the available reaction surface. During formation of the irreversible deposition a hydroperoxide molecule loses ± 4 hydrogen atoms, independent of the degree of deactivation. The rate of deactivation decreases with increasing water concentration and increasing polarity of the solvent. This is attributed to a decreased acid strength of the montmorillonite under these conditions or a reduced deposition due to competitive adsorption of water or the polar solvent molecules. A linear relationship between the montmorillonite activity and the BET surface area appears to exist for the deactivation of Supreme FF in MCT-oil. This relationship has been applied in a simple model, which has been developed in order to describe the kinetics of the disappearance of 13-c,t-HPOD in the presence of deactivation. Regression of the experimental data with the model resulted in statistically significant and physically reasonable values for the apparent activation energies of the conversion and the deactivation which amount to 52 and 38 kJ mol$^{-1}$ respectively.
SAMENVATTING

Veel voedingsmiddelen bevatten vetten en oliën, waarbij de laatste decennia een verschuiving naar het gebruik van plantaardige oliën met hoge gehaltes aan (meervoudig) onverzadigde vetzuren wordt waargenomen. Dit is gerelateerd aan de positieve eigenschappen van deze vetzuren in de reduktie van het risico op hart- en vaatziekten. Een nadeel van onverzadigde vetzuren echter is dat ze gevoelig zijn voor oxidatie, waarbij hydroperoxiden als primaire produkten ontstaan. Hydroperoxiden zijn instabiele verbindingen, die bij ontleding aanleiding geven tot de vorming van krachtige geurcomponenten die het produkt ranzig maken. Ruwe olieën met hoge gehalten aan meervoudig onverzadigde vetzuren bevatten onvermijdelijk kleine hoeveelheden hydroperoxiden, die tijdens raffinage worden geconverteerd door behandeling van de olie met een bleekaarde. Een bleekaarde is een zuur-geactiveerd kleiminaal van het montmorilloniet type. Het inzicht in de chemische processen die plaatsvinden tijdens het bleken is zeer beperkt. Door de conversie van hydroperoxiden te onderzoeken als functie van verschillende procescondities is getracht dit beperkte inzicht te vergroten.

Een literatuuroverzicht wordt gegeven van de chemie van vetzuurhydroperoxiden. Deze worden gevormd via een autokatalytisch oxidatie proces. Wanneer vetzuurhydroperoxiden worden onderworpen aan hogere temperaturen, worden er radicaal reacties geïnitieerd, die leiden tot een complex produktenschaal variërend van splitsingsprodukten, welke over het algemeen de geurcomponenten zijn, vetzure produkten met gewijzigde functionele groepen en oligomeer materiaal. Kennis omtrent zuur-gekatalyseerde ontleding, zoals wordt verwacht op te treden tijdens bleken, is schaars. Splitsing volgens het Hock mechanisme, een algemene reactie voor hydroperoxiden verbonden aan een geconjugeerd systeem, en de vorming van polyhydroxy-componenten is gerapporteerd.
Voor het experimentele onderzoek is gebruik gemaakt van één type vetzuurhydroperoxide: 13-hydroperoxy-9-cis,11-trans-octadecadeheneenzuur (13-c,t-HPOD), welke enzymatisch is bereid. Dit hydroperoxide isomere is één van de vier isomeren die ontstaat tijdens de oxidatie van linolzuur. Hierdoor wordt het produktenscala geminimaliseerd. Door het hydroperoxide te onderzoeken in de vrije vetzuur vorm wordt bovendien de analyse van het reactiemengsel vergemakkelijkt. Als oplosmiddel is gebruik gemaakt van een inert triglyceride, MCT-olie, dat dezelfde fysische eigenschappen als een plantardige olie bezit. Naast dit vetzuurhydroperoxide is tevens cumeen hydroperoxide (CHP) gebruikt. Cumeen hydroperoxide kan worden beschouwd als een model voor meervoudig onverzadigde vetzuren vanwege de analogieën in de structuur, op basis waarvan analoge reacties worden verwacht. Analyse van dit systeem is veel eenvoudiger en omdat geen katalysator deactivering optreedt, kan een uitgebreid kinetisch onderzoek worden uitgevoerd. Bovendien is dit proces interessant vanuit industrieel opzicht, omdat fenol en aceton worden geproduceerd.

De conversies van de hydroperoxiden zijn ladingsgewijs uitgevoerd met verschillende commerciële montmorilloniet katalysatoren variërend in zuursterkte als gevolg van verschillende mate van zuuractivering. De temperatuur is gevarieerd van 273 - 323 K (CHP) of 323 - 413 K (13-c,t-HPOD), met initiële hydroperoxidente concentraties tot 500 mol m⁻³ (CHP) of 60 mol m⁻³ (13-c,t-HPOD) en montmorilloniet concentraties tot 1 kg m⁻³ (CHP) of 10 kg m⁻³ (13-c,t-HPOD). De waterconcentratie is gevarieerd van 2 - 300 mol m⁻³ (CHP) of van 15 - 120 mol m⁻³ (13-c,t-HPOD), en bovendien is het oplosmiddel gevarieerd. Katalysatoren zijn gekarakteriseerd met elementen analyse en N₂-fysisorptie om de mate van deactivering te bepalen.

CHP ontleedt met Filtrol F-20 als katalysator met een selectiviteit van 100% naar fenol en aceton bij 100% conversie en met een vergelijkbare snelheid als in het huidige industriële proces met zwavelzuur als katalysator. De ontleiding verloopt volgens het Hock mechanisme. Water blijkt de katalytische activiteit zeer sterk te remmen. Tijdens de conversie wordt een nieuw bijprodukt, een hydroperoxide ketaal van aceton, gevormd met een selectiviteit tot 25%, wat de ontleidingssnelheid beïnvloedt door de simultane vorming van water. Ontleding van het ketaal vindt eveneens plaats via het Hock mechanisme. 2-phenyl-2-propanol, dat voor ± 5% aanwezig is in industriële voeding, remt de hoofdreactie door de vorming van water via een condensatiereactie van 2-phenyl-2-propanol en cumeen hydroperoxide en door competitieve adsorptie. Katalysatoren met een mindere zuursterkte, zoals ACC FF en XJ-9126, zijn niet in staat cumeen hydroperoxide te converteren onder de toegepaste condities. Een model, gebaseerd op Langmuir-Hinshelwood kinetiek is ontwikkeld om het reactienetwerk van de door F-20 gekatalyseerde conversie in cumeen in het temperatuurgebied van 283 - 313 K kinetisch te beschrijven. Het model bestaat uit 7 adsorptie-evenwichten en 7 andere reactiestappen al dan niet reversibel. Het inhibiterende effect van water kan goed worden ingebouwd middels
een partiële negatieve reactie-orde voor water in de zuur-gekatalyseerde reactiestappen. Regressie van het model aan de experimentele data middels een multirespons Marquardt routine leverde een set van 20 significant geschatte en fysische relevante kinetische parameters, die kunnen worden gebruikt voor reactor ontwerp. De activeringsenergie van de hoofdreductie bedraagt 105 kJ mol\(^{-1}\), terwijl een sterk negatieve partiële reactie-orde voor water van -2.44 is gevonden, overeenkomstig de sterke gevoeligheid van kleikatalysatoren voor de waterconcentratie.


De belangrijkste produkten van de thermisch geinduceerde conversie van 13-c,t-HPOD zijn de splitsingsprodukten hexanal en oxotridecadieenzuur, gevolgd door oxo- respectievelijk hydroxy-octadecadienzuur. Hexanal en oxotridecadieenzuur zijn afkomstig van splitsing van de \(\text{C}_{18}\)-keten aan verschillende kanten van het alkoxy-radicaal afgeleid van het corresponderende hydroperoxide, terwijl disproportionatie met handhaving van de originele stereochemische configuratie een aannemelijk mechanisme voor de hydroxy- en oxo-verbindingen is. De meervoudig onverzadigde reactie componenten zijn gevoelig voor vervolgreacties, het meest waarschijnlijk polymerisatiereacties. De schijnbare activeringsenergie voor thermische conversie bedaagt 91 kJ mol\(^{-1}\), terwijl de invloed van de temperatuur op de selectiviteit zich vooral laat gelden in meer splitsingsprodukten.

Tijdens de Supreme FF gekatalysseerde conversie van 13-c,t-HPOD, die bij een temperatuur van 363 K plaatsvindt op een tijdschaal van enkele ks, worden voornamelijk produkten gevormd, die kunnen worden toegeschreven aan zuur-gekatalysseerde mechanismen. De belangrijkste zijn hexanal en 12-oxo-10-trans-dodecensuur, die worden gevormd via het Hock mechanisme, gevolgd door oxo-octadecadienzuur isomeren als resultaat van een netto dehydratie en octadecatrieenzuur. Bovendien worden produkten gevormd afkomstig van thermisch geinduceerde mechanismes, zoals decadienal en oxotridecadieenzuur. Het meest opmerkelijk aan het netwerk van de montmorilloniet gekatalysseerde onteleding is echter, dat van de produkten ± 80% wordt gevormd via intermediairen, waarvoor dimere componenten met een peroxyde binding zijn voorgesteld. Deze
intermediairen worden langzamer geconverteerd dan 13-c,t-HPOD, maar leveren dezelfde uiteindelijke produkten.

De conversie van 13-c,t-HPOD wordt beïnvloed door het type montmorilloniet; des te sterker zuur, des te sneller de conversie. Bovendien worden met de sterker zuure montmorilloniet typen meer van de geïdentificeerde componenten waargenomen, wat to de conclusie heeft geleid dat de zwakker zuure typen niet in staat zijn de intermediairen te converteren. In tegenstelling tot de algemene trend bij kleigekatalyseerde reacties, heeft de waterconcentratie geen zichtbaar effect op de snelheid van de conversie. De Hock splitsing wordt belangrijker onder droge condities, terwijl bij hogere waterconcentraties meer oxo-octadecadieenzuur wordt gevormd. Bovendien blijken meer polaire oplosmiddelen de conversie enigszins te remmen.

Een belangrijk fenomeen is de extreme deactivering van de montmorilloniet katalysatoren gedurende de conversie van 13-c,t-HPOD. Na een reactietijd van 3 ks bij 363 K in MCT-olie, waarin 13-c,t-HPOD met een initiële concentratie van 30 mol m⁻³ volledig is geconverteerd, bedraagt de mate van deactivering 90%. De deactivering blijkt te verlopen volgens een proces van parallelle deactivering, waarbij materiaal, waarschijnlijk afkomstig van polymerisatiereacties aan het oppervlak, irreversibel wordt afgezet, resulterend in porieblokkade en vermindering van het beschikbare reactie-oppervlak. Tijdens vorming van de irreversibele afzetting verliest een hydroperoxide molecuul circa 4 waterstofatomen, onafhankelijk van de mate van deactivering. De snelheid van deactivering neemt af met toenemende water concentratie en toenemende polariteit van het oplosmiddel. Dit is toegeschreven aan een verminderde zuursterkte van de montmorilloniet onder deze condities of een verminderde mate van depositie door competitieve adsorptie van het water of de polaire oplosmiddelen. Voor de deactivering van Supreme FF in MCT-olie blijkt een lineair verband te bestaan tussen de montmorilloniet activiteit en het BEToppervlak. Dit verband is gebruikt in een eenvoudig model dat is ontwikkeld om de kinetiek van de verdwijning van 13-c,t-HPOD in aanwezigheid van de deactivering te beschrijven. Regressie van de experimentele data aan het model resulteerde in statistisch significante en fysisch relevante waarde voor de schijnbare activeringsenergieën van de conversie en de deactivering, die respectievelijk 52 en 38 kJ mol⁻¹ bedragen.
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</tbody>
</table>

## 9 GENERAL CONCLUSIONS

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## DANKWOORD

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## CURRICULUM VITAE

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NOTATION

Roman symbols

\(a\)  
activity  
mol m\(^{-3}\)

\(a\)  
coefficient to describe water dependency on reaction rate coefficient  
reaction dep.

\(A_{\text{BET}}\)  
BET surface area  
m\(^2\) kg\(^{-1}\)

\(A\)  
pre-exponential factor (Arrhenius)  
reaction dep.

\(A^*\)  
reparameterised pre-exponential factor  
reaction dep.

\(b\)  
parameter estimate  
param. dep.

\(b\)  
coefficient to describe water dependency on reaction rate coefficient  
reaction dep.

\(c_p\)  
heat capacity at constant pressure  
J K\(^{-1}\) mol\(^{-1}\)

\(C\)  
concentration  
mol m\(^{-1}\)

\(C_C\)  
carbon content

\(d_m\)  
diameter of mixer  
m

\(d_p\)  
particle diameter  
m

\(d_{\text{pore}}\)  
average pore diameter  
m

\(D\)  
molecular diffusion coefficient  
m\(^3\) m\(^{-1}\) s\(^{-1}\)

\(D_e\)  
effective diffusion coefficient  
m\(^3\) m\(^{-1}\) s\(^{-1}\)

\(E_{\text{act}}\)  
activation energy  
J mol\(^{-1}\)

\(f\)  
activity coefficient

\(F\)  
ratio of mean regression sum of squares to the residual sum of squares

\(H_0\)  
Hammett acidity

\(\Delta H_r\)  
reaction enthalpy  
J mol\(^{-1}\)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_v$</td>
<td>volumetric reaction rate coefficient</td>
<td>reaction dep.</td>
</tr>
<tr>
<td>$k_w$</td>
<td>specific reaction rate coefficient</td>
<td>reaction dep.</td>
</tr>
<tr>
<td>$K$</td>
<td>equilibrium constant</td>
<td>reaction dep.</td>
</tr>
<tr>
<td>$k_i$</td>
<td>mass transfer coefficient</td>
<td>$m^3 \cdot m^{-2} \cdot s^{-1}$</td>
</tr>
<tr>
<td>$m$</td>
<td>mass</td>
<td>kg</td>
</tr>
<tr>
<td>$m_i$</td>
<td>number of C-atoms in component i</td>
<td></td>
</tr>
<tr>
<td>$M$</td>
<td>molar mass</td>
<td>kg mol$^{-1}$</td>
</tr>
<tr>
<td>$n$</td>
<td>number of moles</td>
<td>mol</td>
</tr>
<tr>
<td>$n$</td>
<td>reaction order</td>
<td></td>
</tr>
<tr>
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<td>number of experimental time sampling points</td>
<td></td>
</tr>
<tr>
<td>$n_{\text{par}}$</td>
<td>number of parameters</td>
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</tr>
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<td>rotation frequency of mixer</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$Nu$</td>
<td>Nusselt number</td>
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<td>peak area</td>
<td>a.u.</td>
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<td>peroxide value</td>
<td>mol m$^{-3}$</td>
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<tr>
<td>$r_v$</td>
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<tr>
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<td>specific reaction rate</td>
<td>mol kg$^{-1} \cdot s^{-1}$</td>
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<tr>
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<td>$S$</td>
<td>selectivity</td>
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<td></td>
</tr>
<tr>
<td>$Sh$</td>
<td>Sherwood number</td>
<td></td>
</tr>
<tr>
<td>$t$</td>
<td>clock time</td>
<td>s</td>
</tr>
<tr>
<td>$t_{(n_{\text{obs}}-n_{\text{par}}, 1-\alpha/2)}$</td>
<td>tabulated $\alpha/2$-percentage point of the t-distribution with nobs-npar degrees of freedom</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$V_{\text{pore}}$</td>
<td>pore volume</td>
<td>m$^3$ kg$^{-1}$</td>
</tr>
<tr>
<td>$X$</td>
<td>conversion</td>
<td>mol mol$^{-1}$</td>
</tr>
<tr>
<td>$Y$</td>
<td>yield</td>
<td>mol mol$^{-1}$</td>
</tr>
<tr>
<td>$Z'$</td>
<td>charge of ionic species</td>
<td>eV</td>
</tr>
</tbody>
</table>
Greek symbols

\( \alpha \) parameter
\( \alpha \) heat transfer coefficient
\( \varepsilon \) molar absorbency
\( \varepsilon_p \) porosity of the catalyst particle
\( \eta \) dynamic viscosity
\( \theta \) fractional surface coverage with component i
\( \lambda \) heat conductivity
\( \rho \) density
\( \sigma^{kl} \) inverse of covariance matrix of the experimental errors of the responses \( C_k \)
\( \sigma \) stoichiometric number
\( \tau \) tortuosity
\( \Phi \) Weisz modulus
\( \Phi \) catalyst deactivation function

Superscripts

obs observed value
^ calculated value

Subscripts

0 initial
av average
b bulk
cat catalyst
i component i, isomer i, reaction i, solute
j component j, solvent
k component k
l component l, liquid
p particle
s surface
t time
tot total
INTRODUCTION

Background

Many food products contain lipids. These lipids, which predominantly are triglycerides derived from vegetables, such as sunflowers, rape seeds, soybeans, olives, etc., contain unsaturated fatty acids, which are susceptible to oxidation reactions (Frankel, 1984). An example of a triglyceride consisting of oleic, linoleic and linolenic acid, which are the most familiar mono, double and triple unsaturated fatty acids, respectively, is depicted in Figure 1.1. Consecutive reactions of the hydroperoxides, which are the primary result of the oxidation reactions, give rise to the formation of undesired flavour components, responsible for the rancidity of the products (Frankel, 1982). The crude oils as received by the refineries already inevitably contain certain amounts of the hydroperoxides and volatile flavour components. One of the goals of the refining process is to remove these hydroperoxides and flavour components and to obtain a purified oil, resistant to renewed oxidation reactions.

![Figure 1.1 Example of a triglyceride, esterified with oleic acid, linoleic acid and linolenic acid (from top to bottom).](image-url)
During refining, edible oils are furthermore purified from many other natural but undesired components present in the raw material, such as free fatty acids, unsaponifiable material, phospholipids, coloured components, metals and solid particles. The conventional refining process consists of several steps which include neutralisation or degumming, bleaching and deodorisation. The latter two steps are relevant with respect to the studies in this thesis.

In the bleaching step, the oil is treated with a bleaching earth. This is an acid activated montmorillonite clay mineral which affects the removal of several of the undesired components, in particular the typical colour components like chlorophyll and carotene, to obtain the desired colourless oil. Furthermore the bleaching earth acts as filter aid. After treatment of the oil, the bleaching earth is filtered off, thereby retaining solid particles. The last and in view of this thesis main purpose is the catalytic removal of oxidised components, predominantly hydroperoxides. Typically, this bleaching is carried out batch wise during 20-30 minutes at a temperature of 70-110 °C with 0.5-2.0% (w/w) of the bleaching earth in suspension. The last step in the refining procedure is the deodorisation, in which by steam distillation at temperatures of 200-240 °C the remaining oxidised components are decomposed and the flavour components, which are the result of the decomposition, are removed.

Objectives and approach

Although the conventional refining process has been applied for decades, not much knowledge about the actual chemical reactions of the oxidised lipids in the latter steps, and especially during bleaching, is available. This knowledge is essential in the research towards milder refining processes, in which the treatment with bleaching earths, which cannot be regenerated, is avoided. The objectives of the studies presented in this thesis therefore are to obtain more insight in the reactions of the hydroperoxides during bleaching and deodorisation: to identify and quantify the reaction products, to elucidate the global kinetics of the reactions and to determine the effect of the process conditions on these parameters.

It is known that fatty acid hydroperoxides react to complex mixtures of products (Frankel, 1985). To avoid even more complex reaction mixtures resulting from oxidised vegetable oils, which consist of mixtures of hydroperoxides, a simplified system has been developed. One isomer of oxidised linoleic acid, 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid (13-c,t-HPOD) has been studied, dissolved in an inert triglyceride oil (Medium Chain Triglyceride oil). The hydroperoxide isomer was used in its free fatty acid form rather than as triglyceride to facilitate the analysis of the reaction products.
For the bleaching earth treatment of fatty acid hydroperoxides furthermore a model system consisting of cumene hydroperoxide as reactant has been studied. This molecule can be considered as a model molecule for polyunsaturated fatty acid hydroperoxides due to the similarities in structure. Both consist of a hydroperoxide group attached to a carbon atom to which furthermore a $\pi$-system is attached, see Figure 1.2, and hence both hydroperoxides are expected to give rise to similar reactions. This model was developed, because of an expected easier elucidation of the reaction network, easier quantification of reaction products, allowing to close the mass balance, and because it appeared that no deactivation occurred, allowing to perform a detailed kinetic investigation. This reaction is furthermore interesting from an industrial point of view, because phenol and acetone are produced by the sulphuric acid catalysed decomposition of cumene hydroperoxide (Gerhartz et al., 1985, 1991), and heterogeneous catalysts such as montmorillonites may provide an alternative (Knifton, 1989).

**Scope of this thesis**

Although not much is known about the reactions of fatty acid hydroperoxides under refining conditions, the reactions of these components at ambient conditions have been studied extensively. A summary of these reactions is presented (Chapter 2) which can be considered as a basis for the subject of this thesis. The main characteristics of clays, especially related to their catalytic properties, are described in Chapter 3.

The results of the kinetic study towards the production of phenol and acetone from cumene hydroperoxide by montmorillonite clays, is presented in Chapter 4. The experimental procedures for the conversion of 13-$c,t$-HPOD and the analytical methods by which the complex reaction mixtures have been identified, both qualitatively and quantitatively, are outlined in Chapter 5.

Chapter 6 describes the thermally induced reaction network of 13-$c,t$-HPOD, discusses potential mechanisms and reveals the influence of several process
The montmorillonite catalysed conversion of hydroperoxides

conditions. The montmorillonite catalysed conversion of 13-c,t-HPOD is subject to extreme deactivation. The effect on the conversion and the catalyst properties are shown in Chapter 7 and a simple kinetic model is presented in order to describe the consequences. The major part of the montmorillonite catalysed reaction network of 13-c,t-HPOD is elucidated in Chapter 8. Mechanisms for the reactions will be proposed and the influence of the main process conditions on the network will furthermore be discussed. Finally, the general conclusions of this thesis will be drawn in Chapter 9.

References

2

FATTY ACID HYDROPEROXIDE CHEMISTRY

2.1 Introduction

Due to the oxidation of unsaturated fatty acids to hydroperoxides and their subsequent conversion to a broad range of products, food products containing these fatty acids may deteriorate under given circumstances. The most relevant chemical reactions responsible for this process and the reactions of the hydroperoxides under the specific refining conditions will be dealt with in this chapter, as far as they were known at the start of the studies described in this thesis.

2.2 Oxidation of fatty acids

2.2.1 Autoxidation

The oxidation of fatty acids takes place at ambient temperatures and atmospheric pressures via the classical autoxidation mechanism. This mechanism is a free radical chain mechanism and consists of initiation, propagation and termination steps as depicted in reactions 2.1 - 2.VI.

initiation: \( \text{RH} \rightarrow \text{R}^\cdot + \text{H}^\cdot \) \hspace{1cm} (2.I)

propagation: \( \text{R}^\cdot + \text{O}_2 \rightarrow \text{RO}_2^\cdot \) \hspace{1cm} (2.II)
\( \text{RO}_2^\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}^\cdot \) \hspace{1cm} (2.III)

termination: \( \text{RO}_2^\cdot + \text{RO}_2^\cdot \rightarrow \) \hspace{1cm} (2.IV)
\( \text{RO}_2^\cdot + \text{R}^\cdot \rightarrow \) stable products \hspace{1cm} (2.V)
\( \text{R}^\cdot + \text{R}^\cdot \rightarrow \) \hspace{1cm} (2.VI)
The montmorillonite catalysed conversion of hydroperoxides

The initiation step is the most difficult step to define since direct hydrogen abstraction from the fatty acid is highly endothermic ($\Delta H^0 = 314-368$ kJ mol$^{-1}$) and therefore very unlikely. A lot of other processes however can initiate the autoxidation, such as reactions with trace metals, irradiation by light, heat and decomposition of hydroperoxides present, which explains the term autoxidation. Once an alkyl radical $R\cdot$ has been formed it reacts very rapidly with oxygen to the peroxy radical $RO_2\cdot$. The second propagation step (2.III) in which the peroxy radical abstracts a hydrogen atom from another fatty acid molecule is potentially the slowest step.

The degree to which a fatty acid is susceptible towards autoxidation depends on the degree of unsaturation. Completely saturated fatty acids are not susceptible to autoxidation. During autoxidation of mono- or polyunsaturated fatty acids relatively stable allylic resp. pentadienylic radicals originate, see Figure 2.1, causing relatively fast autoxidation. Because pentadienylic radicals are more stable than allylic radicals, polyunsaturated fatty acids are more susceptible to autoxidation than mono-unsaturated fatty acids. As a consequence, linoleic acid oxidises 50 times as fast as oleic acid. By autoxidation of linolenic acid two different pentadienylic radicals

Figure 2.1 Mechanism of autoxidation for a: oleic acid, b: linoleic acid and c: linolenic acid. Numbers refer to position of concerned carbon atom.
may originate and this is the reason why linolenic acid oxidises ≈ 2 times as fast as linoleic acid.

Oxygen attacks at either end of the allylic resp. pentadienylic radicals formed. In the case of oleic acid where two different allylic radicals can be formed, the 8- and 10-peroxy radicals are formed from one of the allylic radicals and the 9- and 11-peroxy radicals from the other, see Figure 2.1.a. The peroxy radicals yield hydroperoxides by hydrogen abstraction according to propagation step 2.III. Although only the trans isomers have been depicted, both the cis and trans isomers of each hydroperoxide are formed in ratios depending on the autoxidation conditions. The 8- and 11-hydroperoxy isomers are slightly favoured over the 9- and 10-hydroperoxy isomers, a phenomenon discovered by Frankel et al. (1977a), for which no adequate explanation has been given. In the case of linoleic acid oxygenation of the pentadienyl radical obtained by hydrogen abstraction at C-11 yields the 9-hydroperoxy and the 13-hydroperoxy isomers in equal amounts (Frankel et al., 1977b; Chan and Levett, 1977b). Both positional isomers contain a conjugated diene-structure which may again be present in either the cis,trans or the trans,trans form, the ratio of which is influenced by the autoxidation conditions (Porter, 1980). The formation of the cis,trans isomers is kinetically favoured, especially when hydrogen donating components such as antioxidants are present, while the formation of the trans,trans isomers is thermodynamically favoured (Porter, 1986, 1995).

The oxidation of linolenic acid and higher unsaturated acids is more complex but can be based on linoleic acid as a simple model. The double bond system in linolenic acid for example may be considered as having two separate 1,4-diene systems - the C-9 to 13 system identical to linoleic acid and the C-12 to 16 system. The resulting hydroperoxide mixture contains the cis,trans and trans,trans forms of the 9-, 13-, 12-, and 16-isomers (Chan and Levett, 1977c). The amounts of the 9- and 16-hydroperoxides however are 2-3 times the amounts of the 12- and 13-hydroperoxides. This uneven distribution of isomeric hydroperoxides is caused by a rapid 1,3-cyclisation of the 12- and 13-hydroperoxides to form five-membered hydroperoxyepidioxides, see Figure 2.1.c (Coxon et al., 1981; Neff et al., 1981).

Autoxidation is faster for free fatty acids than for their methyl esters (Miyashita and Tagaki, 1986). Inert fatty acids like stearic acid and acetic acid furthermore appeared to increase the oxidation rate of methyl linoleate and soybean oil, which was explained by a catalytic effect of the carboxyl groups on the formation of free radicals by the decomposition of hydroperoxides (Miyashita and Tagaki, 1986, 1987). When the autoxidation rate of different esters of the fatty acids were compared the following order was observed: triglycerides > diglycerides > methyl ester > monoglycerides (Miyashita and Tagaki, 1988). It was suggested that the intramolecular radical chain reaction is faster than the intermolecular radical chain.
reaction. This also explains that the oxidation of a second acyl group of a triglyceride is faster than the oxidation of the first (Neff et al., 1990).

The autoxidation is inhibited by antioxidants, which are present in oils for example in the form of tocopherols. Their antioxidative ability originates from the presence of a substituted phenol group (AH), which terminates the propagation chain by the following reaction:

$$\text{ROO}^\bullet + \text{AH} \rightarrow \text{ROOH} + \text{A}^\bullet$$

(2.VII)

The chemistry of the effects of antioxidants is rather complex and goes beyond the scope of this thesis.

2.2.2 Photoxidation.

Photoxidation has been subject of interest since light is known to accelerate the oxidation. This is a result of the increased rate of initiation by the formation of radicals resulting from light absorption by species other than lipids. Direct photooxidation, i.e. absorption of light by fatty acids is unlikely to be important because light of the wavelength of absorption (<220 nm) is unlikely to reach the lipids except in direct sunlight in systems without a protective outer layer.

An important process, however, is sensitised oxidation. This process occurs when chemical species called sensitisers, for example chlorophyll, absorb light and sensitise either the unsaturated lipid or molecular oxygen. In the first case R• radicals are formed and the result of photooxidation is the same as that of autoxidation. In the second case singlet oxygen is generated. Singlet oxygen reacts directly with unsaturated lipids by the reaction depicted in Figure 2.2 and does not proceed via a free radical mechanism. This process results in hydroperoxide mixtures different from the autoxidation process. Oleic acid will yield only the 9- and 10-OOH species, predominantly in the trans form (Chan and Levett, 1977a) and linoleic acid can in the case of photooxidation be considered as a molecule with two mono-ene functions and therefore yield the 9-, 10-, 12-, and 13-OOH isomers (Neff and Frankel, 1980). The ratio of the hydroperoxy isomers formed suggests that autoxidation is a competing process. On prolonged photooxidation of polyunsaturated fatty acids cyclic and bicyclic products are formed (Frankel, 1984).
In realistic systems photoxidation is of limited importance, and although many products from photoxidised oxidations are unstable and subject to radical induced decomposition, their decomposition goes beyond the scope of this thesis and will therefore not be considered.

2.3 Isomerisation of hydroperoxides.

The hydroperoxides of linoleic acid readily undergo an isomerisation reaction under mild conditions. A pure isomer like the 13-cis,trans-hydroperoxide kept at 40 °C for 3 days in air will isomerise to all 4 potential isomers, i.e. the cis,trans and trans,trans isomers of the 9- and 13-hydroperoxides (Chan et al., 1979). In this process the O₂ of the hydroperoxide group exchanges with atmospheric oxygen. The reaction has all the properties of a free radical chain reaction. It is for example inhibited by antioxidants. The initial formation of peroxy radicals is again difficult to define since spontaneous generation is unlikely due to high activation energy for the cleavage of the ROO-H bond. It will be discussed in some more detail in the next paragraph. The chain is propagated by the reaction:

\[
RO_2\cdot + R'OOH \rightarrow RO_2H + R'O\cdot
\] (2.VIII)

Mechanistically this propagation starts with the reverse of reaction 2.11., in which the pentadienyl radical is restored and oxygen is liberated, see Figure 2.3. A new attack of oxygen may in the case of linoleic acid subsequently yield all four potential hydroperoxides: two stereoisomers (cis,trans and trans,trans) and two positional isomers (9- and 13-hydroperoxides).

Figure 2.3 Isomerisation mechanism between hydroperoxides.

2.4 Radical induced conversion of fatty acid hydroperoxides

Fatty acid hydroperoxides are rather stable compounds under the right circumstances, such as low temperatures or in the presence of antioxidants. As mentioned before, spontaneous homolysis by either reaction 2.1X or 2.X is very unlikely.

\[
ROOH \rightarrow ROO\cdot + H\cdot \] (2.IX)
\[
ROOH \rightarrow RO\cdot + HO\cdot \] (2.X)
The H-radical removal in reaction 2.IX for example requires a bond-dissociation energy of 378 kJ mol\(^{-1}\) and will only occur via abstraction by another radical. Although the bond-dissociation energy required for the removal of an hydroxy radical in 2.X is much less (185 kJ mol\(^{-1}\)), this process is facilitated by a catalyst like trace metals, or under specific conditions in which the hydroperoxide is subjected to heat or light. Under these conditions also other processes, from which radicals are formed relatively easy, may occur. Examples are the following bimolecular reaction (2.XI) and cleavage of a peroxide (2.XII):

\[
2 \text{ROOH} \rightarrow \text{RO}^+ + \text{RO}_2^- + \text{H}_2\text{O} \quad (2.XI)
\]

\[
\text{ROOR} \rightarrow 2 \text{RO}^+ \quad (2.XII)
\]

Each radical formed may initiate a chain reaction. The chain is propagated by reactions of a radical with a non-radical resulting in a new radical and a new non-radical and is terminated by combination of two radicals to a non-radical molecule. The propagation and termination reactions result in complex mixtures of conversion products which are furthermore complicated by the presence of components which influence these reactions, like oxygen, anti- and pro-oxidants, fatty acids, etc. These components largely influence the rate as well as the selectivity of the conversion. The conversion conditions must therefore be considered when discussing results of experiments. Most research has been performed in the presence of oxygen and often is a combination of autoxidation and decomposition occurring at the same time, making it difficult to determine whether a product is a primary or secondary product.

In the following subparagraphs the relevant reactions described in literature will be summarised with linoleic acid hydroperoxide as example, for which the official name is hydroperoxyoctadecadienoic acid (HPOD). This hydroperoxide has been studied rather extensively and serves, with a few exceptions for some reactions of higher unsaturated fatty acid hydroperoxides, as a model component for all fatty acid hydroperoxides. A distinction is made based on the size of the conversion products formed. The original C\(_{18}\)-hydroperoxide may either cleave to volatile end products, convert to other C\(_{18}\)-components with different oxygenated functional groups or oligomerise. When Frankel et al. (1960) converted linoleic acid hydroperoxide thermally at 210 °C 8-10% volatile, 10% C\(_{18}\)- and 80% oligomeric products were found.

2.4.1 Types of radical reactions

As taken from the review of Gardner (1987) all radical decomposition mechanisms involve one or more of the following reaction types.
Chapter 2  
Fatty acid hydroperoxide chemistry

Radical displacement
Radical displacement as represented by reactions 2.XIII and 2.XIV is a reaction that takes place in almost every mechanism.

\[
\begin{align*}
\text{RH} + \text{X•} & \rightarrow \text{R•} + \text{HX} & \text{(2.XIII)} \\
\text{ROOH} + \text{X•} & \rightarrow \text{ROO•} + \text{HX} & \text{(2.XIV)}
\end{align*}
\]

Reaction 2.III also is an example of this type of reaction. In fact, in the reactions in the figures in which loss or gain of a H-radical is suggested, actually a H-abstraction takes place resulting in displacement of the radical.

Radical combination
Combination of two radicals, such as in reactions 2.IV-2.VI, yields a non-radical product. This process terminates the reaction chain.

Radical addition
By addition of a radical to a double bond a new radical is formed and the chain propagates:

\[
\text{X•} + \text{C=}=\text{C} \rightarrow \text{X-C-C•} \\
\text{(2.XV)}
\]

The autoxidation propagation reaction 2.II is also an addition reaction, for molecular oxygen is a biradical.

Radical elimination
Elimination is the reverse of radical addition:

\[
\text{X-C-C•} \rightarrow \text{X•} + \text{C}=\text{C} \\
\text{(2.XVI)}
\]

Elimination of a peroxy radical leads to isomerisation of the hydroperoxide as described in paragraph 2.3.

Radical disproportionation
Disproportionation is defined as an atom transfer from one radical to another. This yields a saturated and an unsaturated component, see reactions 2.XVII and 2.XVIII.

\[
\begin{align*}
2 \text{CH}_3\text{-CH}_2\text{•} & \rightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{-CH}_3 & \text{(2.XVII)} \\
2 \text{R}_2\text{CH-O•} & \rightarrow \text{R}_2\text{C}=\text{O} + \text{R}_2\text{CH-\text{OH}} & \text{(2.XVIII)}
\end{align*}
\]

The net effect of the disproportionation actually is a H-displacement.
Oxidation-reduction

Oxidation-reduction reactions occur in the presence of transition metals, and actually cannot be captured under the title of this paragraph. Since these metal ions are excellent catalysts for the transformation of hydroperoxides into radicals, it is dealt with shortly. Reduced metal ions react stoichiometrically with hydroperoxides, during which the metal becomes oxidised. Stoichiometric amounts of reduced metal or agents able to reduce the oxidised metal, like cysteine (RSH) or ascorbate, thus have to be applied.

\[
\text{ROOH} + \text{M}^{n+} \rightarrow \text{RO}^\cdot + \text{OH}^- + \text{M}^{(n+1)+} \quad (2.XIX)
\]
\[
\text{M}^{(n+1)+} + \text{RSH} \rightarrow \text{M}^{n+} + \text{RS}^\cdot + \text{H}^+ \quad (2.XX)
\]

Other agents or processes capable of a one-electron abstraction may result in the following reactions:

\[
\text{ROOH} - e^- \rightarrow \text{ROO}^\cdot + \text{H}^+ \quad (2.XXI)
\]
\[
\text{R}^\cdot - e^- \rightarrow \text{R}^+ \quad (2.XXII)
\]

Intramolecular radical rearrangement

This type is a collection of the reaction types mentioned above occurring within one molecule. The formation of epoxides is an example of an intramolecular addition reaction:

\[
(2.XXIII)
\]

The reaction types mentioned above may occur simultaneously and therefore are competitive. The relative importance is determined by the relative reaction rates. Both the peroxy radical and the alkoxy radical are suggested to be the initial radical carriers during the radical induced conversion of fatty acid hydroperoxides.

2.4.2 Volatile products

In spite of the fact that volatiles contribute only to 8-20% of the products of hydroperoxides, most research on the decomposition of hydroperoxides has focused on these products, for they have low flavour threshold values and are the main contributors to the rancidity of oils and fats. Furthermore volatiles are relatively easy to analyse, although quantification is difficult because high temperatures have to be avoided to exclude extra formation of volatiles during analysis. Therefore few papers have been published with reliable quantitative aspects of the formation of volatiles.
The main mechanism for the cleavage of hydroperoxides is the \( \beta \)-elimination. This mechanism starts with the formation of an alkoxy radical according to the reactions described above. Cleavage of the alkoxy radical may occur at either side of the radical, arbitrary designated \( b \) when cleavage takes place between the alkoxy group and the double bond and \( a \) when cleavage takes place at the other side, see Figure 2.4. In the case of 13-HPOD, cleavage \( a \) yields 13-oxo-9,11-tridecadienoic acid (13-OTD) and a C\(_5\)-alkyl radical. This alkyl radical may abstract a hydrogen radical or recombine with a hydroxy radical to give pentane resp. 1-pentanol. Cleavage \( b \) yields hexanal and a C\(_{12}\)-allyl radical which may either abstract a hydrogen radical to form 9,11-dodecadienoic acid or recombine with a hydroxy radical to give 12-hydroxy-9,11-dodecadienoic acid. The latter rapidly isomerises from enol to aldehyde and yields 12-oxo-9-dodecenoic acid.

The \( \beta \)-cleavage mechanism is observed for all allylic hydroperoxides. From 9-HPOD 2,4-decadienal (DD) and octanoic acid will be formed by cleavage \( a \) and cleavage \( b \) will yield 3-nonenal and 9-oxononanoic acid. Since the 9- and 13-hydroperoxy isomers easily interconvert, mixtures of their volatile products are always observed, although in different ratios, if the hydroperoxy isomers are converted in pure form. Frankel (1985) furthermore found that \( \beta \)-scission is more important for cis,trans than for trans,trans hydroperoxides. An overview of the volatiles formed by this mechanism from other hydroperoxides is found in Frankel (1980) and Frankel (1982).

As mentioned in the introduction to this paragraph, the conditions have a large influence on the selectivity of the conversion. Henderson et al. (1980) investigated the influence of time and temperature on the formation of the main volatiles during

Figure 2.4 General mechanism for the cleavage of alkoxy radicals
heating of propyl linoleate in the presence of oxygen. Less hexanal and more decadienal was observed at higher temperatures, see Table 2.1.

The investigators explained this observation by autoxidation of decadienal leading to hexanal at lower temperatures and longer reaction times. Frankel (1982) suggested that the cleavage mechanism shifted from the \( \beta \)-type to the \( \alpha \)-type at higher temperatures. Other investigators found even larger effects of the temperature. Kimoto and Gaddis (1969) for example found that at temperatures below 75 °C 1-2% of the volatiles was decadienal, while at temperatures ranging from 85-210 °C the percentage decadienal ranged from 43 to 72%.

<table>
<thead>
<tr>
<th>Component</th>
<th>65 h at 70 °C</th>
<th>1 h at 180 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexanal</td>
<td>23.7</td>
<td>12.0</td>
</tr>
<tr>
<td>Propyl octanoate</td>
<td>11.8</td>
<td>6.9</td>
</tr>
<tr>
<td>Decadienal</td>
<td>3.5</td>
<td>4.3</td>
</tr>
<tr>
<td>Propyl-9-oxononanoate</td>
<td>14.1</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Although \( \beta \)-elimination explains the largest part of the volatiles formed, typically 85% (Frankel et al., 1981), many more volatiles have been observed. Grosch (1987) has reviewed this subject and mentions a number of 74 volatiles for the hydroperoxides of linoleic acid, including (unsaturated) aldehydes, ketones, alcohols, hydrocarbons and acids, formed under different conditions. The formation mechanism of many of these components has not been elucidated so far.

Not only monohydroperoxides produce volatiles. The volatile fraction found in autoxidised fatty acids is further complicated by the decomposition of unstable secondary oxidation products, like dihydroperoxides, hydroperoxyepidioxides, cyclic peroxides, dimeric peroxides, etc. Many studies have dealt with the decomposition of those individual classes of components, which was reviewed by Frankel (1982).

### 2.4.3 \( C_{18} \)-products

Perhaps the most likely \( C_{18} \)-product to be formed is hydroxyoctadecadienoic acid (HOD). This may be caused by a radical displacement from the alkoxy radical as depicted in Figure 2.5. The readiness with which this reaction takes place is determined by the bond dissociation energy of the weakest X-H bond present. Thus antioxidants with a weak PhO-H bond of <335 kJ mol\(^{-1}\) are susceptible to abstraction by oxy radicals \((RO \cdots)\) to form a stronger RO-H bond of 435 kJ mol\(^{-1}\). Other hydrogens that are susceptible to hydrogen attack are the allylic C-H (368 kJ mol\(^{-1}\)).
ROO-H (± 375 kJ mol\(^{-1}\)) and the methylene bond between two double bonds as in linoleic acid (314 kJ mol\(^{-1}\)).

![Figure 2.5 Radical displacement reaction resulting in formation of hydroxy component.](image)

Although the formation of HOD by this mechanism seems favourable and this reaction occurs significantly for the oxy radical derived from t-butyl hydroperoxide, Gardner et al. (1974) questioned its importance for fatty acid hydroperoxides, because little HOD is usually found. In studies in which larger percentages are found it is often formed in quantities roughly equal to oxooctadecadienoic acid (OOD) (Hamberg et al., 1975). This suggests that radical disproportionation of two oxy radicals is a more dominant mechanism, see Figure 2.6.

This mechanism is supposed to prevail over combination of the radicals due to the polarity of the oxy-radical (Dever and Calvert, 1962). Equal quantities of HOD and OOD were furthermore found for substituted hydroperoxides like epoxyhydroperoxyoctadecadienoic acid (Gardner et al., 1978; Gardner and Crawford, 1981; Gardner and Kleiman, 1981).

![Figure 2.6 Disproportionation of two alkoxy radicals towards hydroxy- and oxodiene](image)

Another mechanism that leads to equal amounts of HOD and OOD is the Russell mechanism (Russell, 1957). Russell studied the autoxidation of ethylbenzene and supported by his kinetic data, proposed the mechanism in Figure 2.7. First two peroxy radicals combine, forming a tetroxide intermediate. Subsequently a complex

![Figure 2.7 Russell mechanism leading to formation of hydroxy- and oxooctadecadienoic acid (HOD and OOD).](image)
rearrrangement takes place leading to the mentioned products and oxygen. Evidence for the Russell mechanism for fatty acid hydroperoxides was reported by Schieberle et al. (1981) who demonstrated oxygen isotope scrambling during the autoxidation of linoleic acid, although this was always less than 1.5%. This low percentage and the fact that the isomeric composition of the HOD and OOD found is not supported by this mechanism suggest that it is of little importance (Schieberle and Grosch, 1981).

Next to monohydroxy components dihydroxy- and trihydroxy components proved to be major products. These are formed thermally (Terao and Matsushita, 1975) as well as in the presence of iron as catalyst (Gardner, 1975). The mechanism for the formation of these products is suggested to proceed via hydroxy radical attack on HOD. This may explain the low concentrations of the monohydroxy-component usually found. From the allylic dihydroxy radical H-displacement yields the dihydroxy and combination with another hydroxy radical results in the formation of the trihydroxy-component. In the presence of oxygen also the hydroperoxy,dihydroxy-component may be formed, see Figure 2.8.

![Figure 2.8 Proposed mechanism for the formation of dihydroxy- and trihydroxy-components (Gardner, 1975).](image)

The hydroxy radical attack is not limited to HOD and probably all components which are di- or higher conjugated are susceptible to this attack.

Oxooctadecadienoic acid (OOD) always is a major product from the conversion of HPOD and is most of the times found in quantities exceeding HOD. Hence, there has to be a mechanism in addition to the disproportionation and the Russell mechanism to explain its formation. A convincing mechanism however is difficult to propose. Hamberg and Gothammar (1975) suggested a reasonable mechanism, see Figure 2.9, although a catalyst like haemoglobin is believed to be essential. In this mechanism OOD is formed by expulsion of a hydroxy radical from the peroxy radical.
Figure 2.9 Mechanism for the formation of oxooctadecadienoic acid (OOD) by Hamberg and Gotthammar (1975).

Another collection of C₁₀-products is the substituted epoxy components formed by an intramolecular addition reaction, see Figure 2.10. This type of reaction has been shown to be a major pathway (Hamberg, 1975; Gardner and Kleiman, 1981). Dobbs et al. (1976) demonstrated that the first step leading to the allylic epoxide radical is reversible. The allylic epoxy radical is susceptible to a variety of combination reactions. If oxygen is present it will react very fast with the allylic radical and a subsequent hydrogen abstraction will yield a hydroperoxide group as X (Gardner et al., 1978). These components then are subject to radical disproportionation, yielding epoxyhydroxy and epoxyoxo components according to the mechanism in Figure 2.10. This was demonstrated by the study of Schieberle et al. (1979), who converted the 13-hydroperoxide from methyl linoleate with the radical initiators Cu²⁺-palmitate or di-t-butylperoxide in the presence of oxygen. If the reaction is carried out under nitrogen in the presence of α-tocopherol, X• may be a tocopheryl radical (Gardner et al., 1972).

Figure 2.10 Intramolecular rearrangement of alkoxy radical to epoxy radical and subsequent radical combination.

Conversions carried out in the absence of oxygen, in the presence of soybean lipooxygenase (Garssen et al., 1976) or haematin (Dix and Marnett, 1983) show that no oxygen is needed to form the epoxyhydroxy component, i.e. the component in which X=OH. It was observed that the original hydroperoxide oxygen atoms were for 70% retained in the molecule and the mechanism in Figure 2.11 was suggested, in which the hydroxy radical is kept in a solvent cage with the alkoxy and the allylic epoxy radical. The role of the lipooxygenase and haematin may be essential in this process making it uncertain to what extent this process occurs in the absence of such components.
The montmorillonite catalysed conversion of hydroperoxides

2.4.4 Oligomeric products

Oligomeric components are the most abundant products of hydroperoxides (Frankel, 1960; Miyashita, 1982a), especially when they are highly concentrated. Depending on the conditions, the oligomeric components are formed by combination or addition reactions and are linked by peroxide groups, as ethers or via a C-C linkages.

Schieberle et al. (1979) and Schieberle and Grosch (1981) found for the conversion of linoleic acid hydroperoxide in the presence of radical initiators, under nitrogen atmosphere peroxidic dimers as major products. They suggested a Russell-like mechanism as depicted in Figure 2.12. Combination of a peroxy radical with a carbon-centred radical is also a possibility since in the absence of oxygen the occurrence of a R• radical is much more likely than in the presence of oxygen:

\[ \text{ROO}^\cdot + \text{R}^\cdot \rightarrow \text{ROOR} \]  \hspace{1cm} \text{(2.XXIV)}

Another mechanism for the formation of peroxide linked dimers is the combination of two alkoxy radicals:

\[ 2 \text{RO}^\cdot \rightarrow \text{ROOR} \]  \hspace{1cm} \text{(2.XXV)}

The three pathways discussed above all yield the same dimer, making it difficult to distinguish between them.
Radical addition reactions may also yield peroxidic dimers, the difference being that during addition reactions the radical chain is propagated and higher molecular weight products may be formed. In Figure 2.13 a general polymerisation mechanism is shown in which in the presence of oxygen a peroxy radical reacts with an unoxidised unsaturated fatty acid to form a peroxy linked dimer (Mayo, 1968). The last component in Figure 2.13 may either abstract an hydrogen atom from another molecule to form a hydroperoxide group or attack a new unsaturated fatty acid by which further polymerisation takes place.

Many investigators however found that the polymerisation of linoleate esters does not progress much beyond the stage of dimers and trimers (Witting et al., 1957; Miyashita et al., 1982a,b). Miyashita et al. (1982a,b, 1984, 1985) also found that these dimers and trimers are already formed during the initial stages of autoxidation. They furthermore identified the dimers formed and found that two linoleate groups were linked via a peroxy group connected by the C-9 or C-13 atoms, with one linoleate part having a conjugated diene function and the other having an ene function on C-10 or C-11 and containing an oxygenated group like a hydroperoxide, hydroxide or keto group, see Figure 2.14. The exact mechanism is not elucidated but starts most probably with a peroxy radical addition to an unsaturated group as shown in Figure 2.13.

Dimers with peroxide bonds however are not very stable at temperatures above 65 °C, supported by the low peroxide content of dimers and oligomers found in thermally treated fatty acids or hydroperoxides. More likely reaction 2.XII is favoured under these conditions.

Ether and carbon linked dimers are much more stable and may be produced by a combination reaction similar to reaction 2.XIII:
The montmorillonite catalysed conversion of hydroperoxides

\[ \text{RO}^\cdot + \text{R}^\cdot \rightarrow \text{ROR} \quad (2.\text{XXVI}) \]

During heating of lipids, fatty acids or hydroperoxides many ether and carbon-carbon linked dimers and oligomers are found (Paulose and Chang, 1978; Williamson, 1953; Frankel et al., 1960). Reaction 2.\text{XXVI} is only one mechanism to explain their formation. In Figure 2.15 a mechanism is depicted which can explain the formation of carbon-carbon linked dimers via a combination mechanism if next to the hydroperoxides also unoxidised fatty acids are present.

![Figure 2.15 Radical combination mechanism to carbon-carbon linked dimers.](image)

Oxy-radical addition to unsaturated acids is another route to dimer production. This addition is expected to be competitive with hydrogen abstraction but results of Minisci (1975) and Pokorny et al. (1976) show that with higher unsaturated fatty acids the oligomeric fraction increases. The importance of oxy-radical addition reactions for which a hypothetical mechanism is shown in Figure 2.16 however is still questionable because no dimers have been identified which would be expected from this type of reaction.

![Figure 2.16 Hypothetical radical addition mechanism to ether linked dimers.](image)
2.5 Acid catalysed conversion of hydroperoxides.

In contrast to the thermal conversion little research has been performed on the acid catalysed conversion of fatty acid hydroperoxides, although this is an important process since during refining raw fats and oils are treated with a bleaching earth, which is a highly acidic solid.

Cumene hydroperoxide (CHP) has been known for over half a century to convert to phenol and acetone by acid catalysis (Hock and Lang, 1944). The conversion is catalysed by both acids of the Brønsted and Lewis type. Kharasch et al. (1950) proposed a heterolytic mechanism for this reaction which basically still holds today, see Figure 2.17 for the mechanism with a Brønsted acid. This mechanism starts with

![Chemical reaction diagram](image)

Figure 2.17 Hock mechanism for the cleavage of linoleic acid hydroperoxide and cumene hydroperoxide.
proton attack on the β-oxygen of the hydroperoxide group. In a concerted mechanism, water is split off and a positively charged epoxide is formed as intermediate. By a subsequent rearrangement the phenyl-carbon linkage is broken, resulting in the formation of an ether with the positive charge located on the neighbouring carbon atom. This process is rate determining. The following reactions: attack of water and release of a proton, a new proton attack on the ether oxygen, release of phenol and deprotonation to form acetone all proceed very rapidly.

Since then the acid catalysed conversion of many more organic hydroperoxides have been studied and the Hock cleavage appeared to be an important route for most of the hydroperoxides (Hiatt, 1971). It is known now that the reaction rate depends on the group neighbouring the carbon atom to which the hydroperoxide is connected: cyclobutyl > aryl >= vinyl > hydrogen > cyclopentyl, cyclohexyl >> alkyl. Thus the reaction rate expected from this order for cumene hydroperoxide and linoleic acid hydroperoxide are among the highest and are close to each other.

Grosch et al. (1981) and Gardner and Plattner (1984) reported this type of cleavage for fatty acid hydroperoxides in aprotic solvents, see left half of Figure 2.17. This way hexanal and 12-oxo-10-dodecenoic acid (ODE) are formed from 13-HPOD and 2-nonenal and 9-oxononanoic acid from 9-HPOD. Gardner and Plattner (1984) even found 100% selectivity to these products when boron trifluoride, a Lewis acid, was used as catalyst in ether as solvent.

\[
\begin{align*}
\text{OH} & \quad + \text{H}^+ \quad \rightarrow \quad \text{OH} \quad + \text{H}_2\text{O} \\
\text{OH} & \quad + \left[ \begin{array}{c}
\text{OH} \\
\text{OH}
\end{array} \right] \quad + \text{H}^+ \quad \rightarrow \quad \text{OH} \quad \text{OH} \\
& \quad + \text{OH}
\end{align*}
\]

Figure 2.18 Acid catalysed mechanism towards epoxyhydroxy and trihydroxy components.

When HPOD was converted in a protic solvent by Brønsted acids, very little cleavage was observed and the main products were epoxyhydroxy and trihydroxy components as was found by Gardner et al. (1984a), who converted linoleic acid in water with sulphuric acid as catalyst. The products were formed by the mechanism shown in Figure 2.18, which proceeds via a positively charged allylic epoxide. The component between brackets has not been observed, but the presence of its solvolysis product indicates its presence as an intermediate, which appeared to be very unstable towards acids. If methanol was present as solvent predominantly methoxy groups were found instead of hydroxy groups (Gardner et al., 1984b).
Kimoto and Gaddis (1969, 1974) determined the selectivity towards aldehydes during treatment of autoxidised fatty acids or oils with activated clays and found selectivities of 8% for oxidised methyl linolenate, 22-35% for oxidised methyl linoleate and 66% for oxidised methyl oleate. Thus less cleavage appeared to occur for higher unsaturated fatty acids. The main aldehydes from the treatment of methyl linoleate were hexanal (53-70%), 2-nonenal (23-31%) and pentanal (10-12%). No dienals were observed. These results, except for the formation of pentanal can easily be explained by the Hock cleavage as depicted in Figure 2.17.

Not much information is available on the kinetics of the acid catalysed conversion of fatty acid hydroperoxides. Tokita and Morita (1985) investigated the individual conversion rates of the 4 HPOD-isomers in acetone : water 9 : 1 by 0.1M HCl and remarkably found that the trans,trans isomers converted more rapidly than the cis,trans isomers. The conversion was furthermore first order with respect to the hydroperoxide, was fastest at low water concentrations and decreased with respect to solvent in the following order: methanol > ethanol > acetone > dimethylsulfoxide > tetrahydrofuran. The apparent activation energy amounted to 92 kJ mol$^{-1}$ and was equal for all isomers. Additionally, 2-nonenal and 12-oxo-10-dodecenooate were formed predominantly from the cis,trans- over the trans,trans-isomers of the 9- and 13-hydroperoxy components, a phenomenon for which no explanation was presented.

Boki et al. (1989) more practically studied the decrease in peroxide content when autoxidised soybean oil was filtered over different types of clays and oxides and found a good relation between the decrease in peroxide content and the concentration of acid sites with a Hammett acidity <1.5. Due to the large amounts of filter material used no conclusions can be drawn to whether adsorption or catalysis was the dominant process.

2.6 Conclusions

Polyunsaturated fatty acids are susceptible to autoxidation upon which hydroperoxides are formed as oxidation products. The autoxidation rate depends on many factors and is for example accelerated by light and inhibited by antioxidants. By autoxidation a complex mixture of stereoisomers and positional isomers of the hydroperoxides of the different unsaturated fatty acids present is formed.

Hydroperoxides are converted by thermally induced radical reactions, by which a broad range of products is formed. Cleavage of the C$_{18}$-chain leads to the production of volatile components, responsible for the rancidity of the oil if this process occurs after refining. Conversion of the hydroperoxides may also lead to C$_{18}$-products with different oxygenated groups such as ketones and alcohols. The main fraction however usually consists of oligomeric products linked as peroxide, as ether or via a carbon-carbon bond.
The acid catalysed conversion of fatty acid hydroperoxides in aprotic solvents by either Brønsted and Lewis acids leads amongst other reactions to cleavage of the C₁₈-chain according to the Hock-mechanism. In protic solvents and with Brønsted acids polyhydroxy components are found as main products.

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3

CLAY CATALYSTS

3.1 Introduction

Clay minerals are solids with a layered two-dimensional structure and are found in many different forms. Clays are used in a variety of applications including decolorisation, purification, stabilisation, adsorption, binding, as filler and as catalyst. The latter application arises from the acidity of the minerals. In the next paragraphs the most important physical and chemical properties of these type of minerals will be discussed with respect to their catalytic applications.

3.2 Physical properties of clay minerals

Due to its layered two-dimensional structure, clay minerals are also called phyllosilicates. The building blocks of clay minerals are the tetrahedral Si(O,OH)$_4$ and the M(O,OH)$_6$ octahedra with M = Al$^{3+}$, Mg$^{2+}$ or Fe$^{2+,3+}$. The condensation of a monolayer of tetrahedra (T) with a monolayer of octahedra (O) gives the 1:1 or TO minerals known as kaolinites with M = Al$^{3+}$ or serpentines when M = Mg$^{2+}$. When a monolayer of octahedra is sandwiched between two layers of tetrahedra 2:1 or TOT minerals are obtained. The clay is called dioctahedral in the case of Al-octahedra and trioctahedral for Mg-octahedra. In the former case two out of three octahedral sites are occupied, in the latter case all three are occupied.

The ideal structure of a 2:1 clay mineral is electroneutral and is found in nature as pyrophyllite (dioctahedral) or talc (trioctahedral). If isomorphous substitution of Si$^{4+}$ in the tetrahedral layer or Al$^{3+}$ and Mg$^{2+}$ in the octahedral layer has occurred other mineral types are obtained with different properties. This substitution for ions with a lower charge results in a negatively charged lattice. The electrical neutrality is
The montmorillonite catalysed conversion of hydroperoxides

maintained by the presence of exchangeable cations. The general formula representation of is then: \((\text{Si}_{8-x}\text{M}_x)^{IV} (\text{Al}_{4-y}\text{M}'_y)^{VI} (\text{OH})_4 \text{O}_2 \text{M}^{n+}_{(x+y)/n} \text{mH}_2\text{O}\) for dioctahedral clays and: \((\text{Si}_{8-x}\text{M}_x)^{IV} (\text{Mg}_{6-y}\text{M}'_y)^{VI} (\text{OH})_4 \text{O}_2 \text{M}^{n+}_{(x+y)/n} \text{mH}_2\text{O}\) for trioctahedral clays. The superscripts IV and VI refer to the tetrahedral and octahedral layers respectively. \(\text{M}\) and \(\text{M}'\) have one unit of charge less than the cation they replace and \(\text{M}''\) is the exchangeable cation with valence \(n\). Generally three groups are distinguished depending on the degree of isomorphic substitution. For the smectites, which is the main group: \(x + y = 0.25 - 0.6\), corresponding to a cation exchange capacity (CEC) of 0.64 - 1.5 meq g\(^{-1}\). Isomorphous substitution is mainly localised in the octahedral layer. This results for dioctahedral resp. trioctahedral smectites in montmorillonites and hectorites. If however isomorphous substitution is localised in the tetrahedral layer, the minerals are called beidellite (dioctahedral) resp. saponite (trioctahedral). The catalyst used in the studies described in this thesis are of the montmorillonite type for which the ideal formula is: \((\text{Si}_8 (\text{Al}_{3.15}\text{Mg}_{0.85}) \text{O}_{20} (\text{OH})_4 \text{X}_{0.85} \text{mH}_2\text{O}\). The complete classification of 2:1 clay minerals is shown in Table 3.1.

**Table 3.1 Classification of 2:1 clay minerals**

<table>
<thead>
<tr>
<th>Charge/formula</th>
<th>Group</th>
<th>Subgroup</th>
<th>Isomorphous substitution of</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Pyrophyllite</td>
<td>Dioctahedral</td>
<td>Pyrophyllite</td>
<td>Talc</td>
</tr>
<tr>
<td>0.25 - 0.6</td>
<td>Smectite</td>
<td>Dioctahedral</td>
<td>Al(^{3+})</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Si(^{4+})</td>
<td>Beidellite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trioctahedral</td>
<td>Si(^{4+})</td>
<td>Saponite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mg(^{2+})</td>
<td>Hectorite</td>
</tr>
<tr>
<td>0.6 - 0.9</td>
<td>Vermiculite</td>
<td>Dioctahedral</td>
<td></td>
<td>Vermiculite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trioctahedral</td>
<td></td>
<td>Vermiculite</td>
</tr>
<tr>
<td>1</td>
<td>Mica</td>
<td>Dioctahedral</td>
<td></td>
<td>Muscovite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trioctahedral</td>
<td></td>
<td>Biotite</td>
</tr>
</tbody>
</table>

The distance between two TOT layers is variable and depends on the size of the exchangeable cation and on the type and amount of solvent present in the interlamellar space. Therefore most of the smectites are swellable causing an increase in the distance between two sheets from 1.25 nm when a monolayer water is present, via 1.55 for a bilayer of water to 1.8 nm in case of three water layers, see Figure 3.1. The presence of water between the layers solvates the exchangeable cations. When a clay is dehydrated to water contents of less than 5% (w/w) the remaining water is believed to be chemically adsorbed. On further dehydration, which may be achieved at temperatures above 200 - 400 °C, the clay structure may collapse, making the interlamellar space inaccessible. The interlayer space is
Chapter 3 Clay catalysts

Figure 3.1 Swelling of the clay by water leading to an increase in the interlamellar distance.

responsible for the microporous character of the clay minerals and may be fixed by the process of pillaring (Schoonheydt, 1991). Next to the microporosity the clay consists of mesopores due to a cardhouse like structure of the layers each consisting of typically 5-10 TOT layers (McCabe, 1992).

The thermal instability mentioned above is the main drawback of clays compared to zeolites, most of the other properties like the catalytic activity being similar and the larger average pore size of a clay often is a major advantage. Therefore much research has been carried out in developing more stable clay catalysts by pillaring of the layers. This way a stable three-dimensional structure originates.

3.3 Chemical properties of clay minerals

Figure 3.2 Structure of Brønsted and Lewis acid sites.

Clay minerals owe their catalytic activity to the presence of acid sites, both of the Lewis and Brønsted type, which are present as shown in a simplified structure in Figure 3.2. Brønsted acid sites are present, due to the previously discussed electronegative charge of the lattice structure. This negative charge may be compensated by protons, which exhibit Brønsted acidity, but more importantly the negative charge may be compensated by other exchangeable cations which may exert a polarising effect on the solvated water, resulting in dissociation of the solvated water and a ready release of a proton:

\[
[M(H_2O)_m]^{n+} \rightleftharpoons [M(OH)(H_2O)_{m-1}]^{(n-1)+} + H^+ \quad (3.1)
\]
The protonic acid sites are located both at the external surface as in the interlayer region. Lewis acidity comes from electron deficient sites, see Figure 3.2, located at the edges of the clay layers.

The acidity of a solid is determined by the amount and the strength of the sites present. The amount is expressed by the number of sites per weight unit of solid. The acid strength is more difficult to define. The Hammett acidity $H_0$ as developed by Hammett and Deyrup (1932) is mostly used for solid acids and is the ability of a proton to convert an adsorbed neutral base into its conjugated acid, quantitatively described by:

$$H_0 = -\log \frac{\alpha_{H^+} f_B}{f_{BH^+}} = pK_a + \log \frac{C_B}{C_{BH^+}}$$  \hspace{1cm} (3.1)

In this equation $\alpha_{H^+}$ represents the activity of the protons and $f_B$ and $f_{BH^+}$ are the activity coefficients of the base and its conjugated acid. $pK_a$ is the acid dissociation constant. For the determination of the acid strength of a solid, a set of indicators with known $pK_a$-values can be used. If an indicator shows its acid colour when it is adsorbed on the solid, acid sites with a Hammett strength smaller then the $pK_a$-value of the indicator are present. The Hammett acidity is also used for concentrated mineral acids and for the determination of acids in organic solvents. From Equation 3.1 it is easily deduced that for dilute aqueous solutions, where $f = 1$, $H_0$ equals the $pH$.

**Table 3.11** Acid strength of some clay minerals as measured using Hammett indicators.

<table>
<thead>
<tr>
<th></th>
<th>$H_0$ value ($pK_a$ range of strongest acid sites)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-3.0 to -5.6</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>-3.0 to -5.6</td>
</tr>
<tr>
<td>Palygorskite</td>
<td>+1.5 to -3.0</td>
</tr>
<tr>
<td>Talc</td>
<td>+3.3</td>
</tr>
</tbody>
</table>

Values under A and B are taken from Benesi (1956) and Fowkes et al. (1960). They refer to samples as received and after drying at 120 °C for 16 hours, respectively. Values under C are from Solomon et al. (1971) with near-zero water content.

Table 3.11 shows the acid strength of the strongest sites of several clay minerals and reveals the differences between the different types (Theng, 1982). Kaolinite and montmorillonite are amongst the types with the strongest acidity and represent an acid strength comparable with sulphuric acid concentrations up to 90%. This value shows that clay minerals are very active with respect to many acid catalysed reactions (Taylor and Jenkins, 1988; Ballantine et al., 1983).
However, in amorphous or semicrystalline solids, protons of variable acid strength are present due to differences in the local structure surrounding the proton. If information concerning both the amount and strength is combined, an acid strength distribution is obtained, which gives the more detailed information. This information may be determined by titrations developed by Benesi (1957). In Figure 3.3 the acid strength distribution of a typical Filtrol clay, a commercial acid activated clay, is compared to distributions of other mixed oxides (Benesi, 1978).

Figure 3.3 shows that Filtrol has less acid sites than SiO$_2$-MgO but that the sites of Filtrol are stronger. SiO$_2$-Al$_2$O$_3$ contains more and stronger sites than Filtrol. Rupert et al. (1987), in contrast, found 0.55 mmol protons per gram of catalyst with $H_0$<-3.0, which is 5 times as many as Benesi found. This difference may be due to clays taken from different sources or with different treatments.

3.3.1 Acid activation and cation exchange

A way to modify the chemical properties of a clay, including its acidic properties is by replacing the natural exchangeable cations, such as Na$^+$ or Ca$^{2+}$, for strong polarising cations (Purnell, 1990). As a result of the strong polarising ions, the most effective being Al$^{3+}$, Fe$^{3+}$ or Cr$^{3+}$ (Adams et al., 1983), a stronger acidity is obtained, since the solvated ion on the right hand side of reaction 3.1 becomes more stable and the equilibrium shifts to the right. As a consequence the protons are more active. The exchange is easily achieved by treating the clay with a solution containing the desired cations, for these highly valenced cations are much more tightly bound. Table 3.11 shows an example of the influence of the exchangeable cation on the acid strength of the smectite as determined by Rupert et al. (1987).
The montmorillonite catalysed conversion of hydroperoxides

Table 3.11 Acid strength of smectites.

<table>
<thead>
<tr>
<th>Smectite</th>
<th>$H_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$-montmorillonite</td>
<td>+1.5 - -3.0</td>
</tr>
<tr>
<td>NH$_4^+$-montmorillonite</td>
<td>+1.5 - -3.0</td>
</tr>
<tr>
<td>H$^+$-montmorillonite</td>
<td>-5.6 - -8.2</td>
</tr>
<tr>
<td>acid activated clay</td>
<td>&lt; -8.2</td>
</tr>
</tbody>
</table>

This table shows that although a natural clay like the Na$^+$-form contains reasonable acidity, proton exchanged or acid treated smectites show acidity with a Hammett-strength down to values lower than -8.2 which is comparable to 90% concentrated sulphuric acid.

Another more rigorous way to enhance the activity of clays is by treatment with a mineral acid, which is carried out for most applications. This treatment dissolves the lattice-Al starting at the edges of the layer and results in a more open and accessible structure. The BET-area generally increases tenfold up to values of 500 m$^2$·g$^{-1}$ (van Olphen, 1968). This increase is predominantly ascribed to an increase in the mesoporosity of the mineral as a consequence of an increase in the cardhouse like structure. Additionally the natural exchangeable cations are replaced for protons and Al ions which have been dissolved from the lattice. So the treatment results in more and more accessible acid sites of higher acid strength, see Figure 3.4.

![Figure 3.4 Acid activation of clay minerals.](image)

When the clay is acid activated or when the natural exchangeable cations have been replaced for strong polarising ions, the clay is able to catalyse reactions below 100 °C, provided they proceed via tertiary or allylic cations. At 150-180 °C reactions involving primary or secondary carbocations are possible (Adams et al., 1983).

3.3.2 Influence of water

Water has a dramatic negative influence on the acid activity of the clay. This is caused by shielding of the protons and metal ions, thereby dissipating the proton charge and the polarising effect of the metal ions. Reaction 3.1 thus proceeds more readily with smaller x.
In Table 3.11 it was already shown that the pre-treatment of the clay, i.e. the degree of drying of the clay, affected the acid strength of the strongest sites. Solomon et al. (1971) furthermore quantified this effect for a kaolinite clay mineral and found a dramatic increase in the $H_0$ value with increasing free water content, see Figure 3.5. Going from a dried clay to a water content of 1% the Hammett strength already decreased from $<-8.2$ to -3. At 10% water content only weak acid sites of $H_0=3$ are present.

3.3.3 Influence of solvent

The shielding of the proton acidity also occurs to a lesser extent in other polar solvents like alcohols, acids and ketones (Rhodes and Brown, 1994). Solomon et al. (1971) for example found that the $H_0$ range of the dry kaolinite clay increased from $<-8.2$ in dioxan via -3.0 to -5.6 in ethyl acetate to 3.3 to 4.0 in ethanol.

For reactions carried out in the liquid phase involving tertiary carbocations the most suitable solvents are those that provide good miscibility, like 1,4-dioxan. More acid conditions required for the other reactions are reached in more non-polar solvents (Adams et al., 1983).

3.4 Conclusions

Clays are solids with a two-dimensional layered structure. Due to a natural replacement of the structural ions by ions with a lower valence, the structure is electronegative, which is compensated by exchangeable cations. Next to these ions water is present between the layers. The amount of water determines the interlayer distance. Clays behave as strong acids if the exchangeable cations are protons or if the cations may generate protons by a strong polarising power on solvated water. This situation may be created by cation exchange or acid activation.

References

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THE MONTMORILLONITE CATALYSED PRODUCTION OF PHENOL AND ACETONE FROM CUMENE HYDROPEROXIDE

4.1 Introduction

The industrial production of phenol and acetone mainly takes place by the acid catalysed decomposition of cumene hydroperoxide, which is formed by oxidation of cumene. Hock and Lang (1944) invented this process in 1944 and in 1952 the first production plant was put in operation. Nowadays 90 % of the phenol and 70 % of the acetone production proceeds via this route (Gerhartz et al., 1985, 1991). The decomposition is typically carried out at atmospheric pressure and temperatures from 348 to 368 K with acetone as solvent with 0.1 to 2 % w/w sulphuric acid.

The oxidation of cumene is performed with molecular oxygen and is autocatalytic, analogous to the autoxidation of unsaturated fatty acids, see paragraph 2.2.1. As by-products 2-phenyl-2-propanol, acetophenone and minor amounts of dicumyl peroxide are formed. These by-products are also fed to the plant in which cumene hydroperoxide is decomposed to phenol and acetone. Next to sulphuric acid other strong mineral acids such as sulphur dioxide and perchloric acid are employed as catalyst, and in Russia also acidic ion exchangers are used. The selectivity obtained is usually high, but due to the presence of 2-phenyl-2-propanol, some dicumyl peroxide, α-methyl styrene and dimers are formed together with minor by-products as mesityl oxide, cumyl phenols and cumyl phenyl ether. Patents have appeared which specifically claim to decompose the dicumyl peroxide to the desired products.
phenol and acetone, along with α-methyl styrene as by-product (Sifniades et al., 1982). α-methyl styrene is distilled off downstream of the reactor and is either reduced to cumene, which subsequently can be added to the feed for the oxidation step, or used for other purposes (Gerhartz et al., 1991).

Although the decomposition step with mineral acids is fast and selective and only little corrosion occurs, heterogeneous catalysts can achieve the same or better activity and selectivity without any corrosion. Heterogeneous catalysts have the advantage that less process steps are necessary, because the separation of the catalyst is much easier. Many solid acids have been claimed in the patent literature as potential catalysts for the production of phenol and acetone, including zeolites (Romana et al., 1986; Knifton and Dai, 1991), heteropoly acids or acidic ion exchangers (Knifton and Sanderson, 1990), clays (Knifton, 1989a), mineral acids deposited on inert carriers (Knifton and Grice, 1989) and combinations of these solid acids (Knifton and Sanderson, 1990; Knifton 1989b). A kinetic investigation however is still missing in the open literature. This chapter reports on such a study with a montmorillonite clay as catalyst. Preliminary results of this investigation were presented at the 11th World Congress on Catalysis (De Groot et al., 1996).

4.2 Experimental and analytical procedures

4.2.1 Materials

Cumene hydroperoxide (CHP) of technical quality was obtained (Sigma, ± 80 %) and was purified by procedures based on Hock and Lang (1944) and Fil'makova et al. (1974). The CHP of technical quality (100 ml) was diluted with 250 ml cumene (Janssen 99%) and the mixture was washed with 100 ml of a 1% NaOH solution to remove acidic impurities. Subsequently 100 ml of a 30% NaOH solution was slowly added to the CHP dilution, which was brought at a temperature of 0 °C. The crystals of the sodium salt of the hydroperoxide formed were filtered off and washed with dichloromethane. The salt was dissolved in 400 ml distilled water and the solution was carefully neutralised with 1N HCl. The two phases were separated and the water phase was washed with 100 ml dichloromethane. The combined organic layers were washed thoroughly with water and dried over sodium sulphate. The dichloromethane was removed by purging nitrogen through the solution. The resulting purity was 99 %, the other 1 % predominantly being cumene. The latter was employed as solvent during the kinetic experiments and therefore did not constitute a problem. Phenol (PH), dicumyl peroxide (DCP), acetophenone (ACP), 2-phenyl-2-propanol (PP), α-methyl styrene (AMS) (all from Aldrich), cumene (CUM) (Janssen, 99%) and acetone (AC) (Merck, p.a.) were obtained in the highest purity available and used as received.
The highly activated montmorillonite clay Filtrol Grade F-20, kindly made available by Engelhard was chosen as main catalyst. Next to F-20 also XJ-9108 and XJ-9126 from Engelhard and Supreme FF and ACC FF from Südchemie were used. The physical properties of the catalysts used are shown in Table 4.1. To avoid potential transport limitations the catalyst was sieved and the fraction of particles with a diameter smaller than 38 µm was used for the kinetic experiments. The volume averaged catalyst diameter was 20 µm as measured by the Coulter LS 130 apparatus. The catalyst was dried at 1 bar and 363 K during 16 hours before use in order to obtain reproducible water contents.

| Catalyst   | Supplier      | Acidity      | Use            | BET-surface area [m² g⁻¹] | Pore Volume [cm³ g⁻¹] | Pore diam [nm] |
|------------|---------------|--------------|----------------|---------------------------|-----------------------|----------------|------------------------------------------------|
| F-20       | Engelhard     | Strong       | General        | 286                       | 0.335                 | 5.4            |
| XJ-9108    | Engelhard     | Strong       | General        | 321                       | 0.364                 | 5.0            |
| XJ-9126    | Engelhard     | Medium/Strong| Bleaching      | 314                       | 0.444                 | 6.0            |
| Supreme FF | Südchemie     | Strong       | Bleaching      | 321                       | 0.461                 | 6.1            |
| ACC FF     | Südchemie     | Medium       | Bleaching      | 190                       | 0.277                 | 6.3            |

4.2.2 Procedures

Reaction procedure and conditions
Reactions were performed in a thermostated batch reactor of 100 cm³ under nitrogen atmosphere with cumene as solvent. In a typical experiment solvent was pipetted in the reactor and the reactor was brought at the designated temperature. The reactor was brought under nitrogen by repeatedly switching between vacuum and nitrogen atmosphere. Reactant(s) and toluene, which was used as internal standard, were added in the required quantities, while a small overpressure of nitrogen was maintained to avoid introduction of oxygen. A sample was taken by a syringe punctured through a septum and subsequently catalyst was added, marking the start of the experiment. At suitable intervals samples were taken from which the catalyst

<table>
<thead>
<tr>
<th>Table 4.11 Range of experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Main solvent</td>
</tr>
<tr>
<td>Main catalyst</td>
</tr>
<tr>
<td>Batch time</td>
</tr>
<tr>
<td>$C_{cat}$</td>
</tr>
<tr>
<td>$C_{CHP,0}$</td>
</tr>
<tr>
<td>$C_{AC,0}, C_{PH,0}$</td>
</tr>
<tr>
<td>$C_{PP,0}, C_{AMS,0}, C_{DCP,0}, C_{ACP,0}$</td>
</tr>
<tr>
<td>$C_{H2O,0}$</td>
</tr>
</tbody>
</table>
was removed by syringe filters. The range of experimental conditions covered for this investigation is shown in Table 4.11. Reactions were performed with single components as well as with combinations of cumene hydroperoxide with one of the other components. Blank experiments showed that a mixture of cumene, acetone and phenol did not undergo any reactions. No reactions were observed in the absence of catalyst. Next to cumene and Filtrol F-20 also the solvents heptane, toluene, acetone, phenol/acetone, ethyl acetate and ethanol and the catalysts Supreme FF, ACC FF, XJ-9126 and XJ-9108 were applied.

Experiments in which cumene hydroperoxide was repeatedly added to the reactor, using the same batch of catalyst, showed that the disappearance rate decreased a little on every new batch of cumene hydroperoxide, but it was concluded that for a single batch deactivation of the catalyst could be neglected. Theoretical calculations, see the Appendix to this Chapter, and experiments with catalysts with varying average particle diameter showed that experiments were in the intrinsic kinetic regime, i.e. were not influenced by transport phenomena.

HPLC-UV analysis
For the quantitative analysis of the components in the reaction mixture a HPLC method has been developed. Samples diluted to appropriate concentrations were separated over a reversed phase column (Zorbax ODS-2, 150x4.6 mm, 5 μm particles) with gradient elution of 1 ml min⁻¹ acetonitrile/water mixtures. This gradient started with 15 % acetonitrile for 1 minute and was subsequently raised to 100 % during the next 20 minutes, where it was kept for another 4 minutes. Detection and quantification was performed by UV absorption at 254 nm. In Figure 4.1 a typical chromatogram is shown, indicating the good separation obtained. The components eluted in the following order (retention times in minutes): acetone (2.3), phenol (7.7),
2-phenyl-2-propanol (9.8), acetophenone (10.5), cumene hydroperoxide (11.3), toluene (15.3), α-methyl styrene (17.0), cumene (18.0), dicumyl peroxide (20.8), bis-cumylperoxy-acetone ketal (BCAK) (21.7) and the α-methyl styrene dimers (DIM) (21.9, 22.4 and 22.6, not shown). Calibration factors were obtained easily for all components except BCAK and the α-methyl styrene dimers, which are not commercially available. Quantification of the total amount of these dimers was done by assuming 100 % selectivity of the reaction of pure α-methyl styrene to its dimers, as the HPLC-chromatogram was free of other components. For the quantification of BCAK the calibration factor of dicumyl peroxide was used.

Identification of BCAK by HPLC-MS.
Identification of bis-cumylperoxy-acetone ketal (BCAK) was performed by HPLC with on-line MS detection (Fisons Trio2000 apparatus, MassLynx software). The HPLC conditions were identical to the conditions used for HPLC-UV. Two ionisation techniques were used. On ElectroSpray (ES) ionisation the post column flow of 1 ml/min was split in a ratio 1:50 and to the resulting 20 μl min⁻¹ was added 10 μl min⁻¹ of 30 mM ammonium acetate in acetonitrile/water (1/1) to enable the formation of (M + NH₄)⁺ adducts. A capillary voltage of 4.2 kV and a cone voltage of 24 V were applied at a temperature of 60 °C. Particle beam Electron Impact (EI) ionisation with an electron energy of 70 eV was employed to obtain fragmentation patterns.

The structure of the component with the tentative name bis-cumylperoxy-acetone ketal (BCAK) as proposed in Figure 4.2 was, amongst other indications, based on the molecular mass of 344 a.u. This had been revealed by HPLC-MS with ElectroSpray detection. Electron Impact ionisation showed a fragmentation pattern, with m/z-ratios of 119 and 135 being dominant, which may be attributed to the following structures: Ω-C(CH₃)₂⁺ and Ω-C(CH₃)₂-O⁺, which indeed are part of BCAK. The apolar structure of BCAK is in agreement with the relatively large retention time, comparable to dicumyl peroxide and the α-methyl styrene dimers. Other mechanistic considerations as that upon formation of one molecule of the component, one molecule of water is formed and two molecules of cumene hydroperoxide and one molecule of acetone are consumed, see paragraph 4.3.1, are furthermore also in line with the proposed structure.

The quantification of BCAK was performed based on the calibration factor of dicumyl peroxide, because both these molecules consist of phenyl groups with an isopropylperoxy structure attached. These structural aspects predominantly determine the molar absorbency and therefore equal molar absorbencies were expected. This assumption appeared to be reasonable since the calculated amount
of BCAK based on this assumption was equal to the increase in the water concentration as well as to the difference between the acetone and phenol concentration and allowed to close the mass balance.

Karl-Fischer analysis.

Water concentrations were determined by automatic Karl-Fischer coulometric titrations, performed on a Metrohm 684 KF Coulometer with a 703 titration stand. The water concentration could be measured the least accurately due to the low water concentrations, causing large relative errors. Furthermore it appeared to be very difficult to set the initial water concentration, due to differing humidity of the reactants.

4.2.3 Parameter estimation

The regression of the experimental data was based on the maximum-likelihood criterion, as outlined by Froment and Hosten (1981). Parameter estimates were obtained by applying the least squares criterion to the observed reaction mixture component concentration, \( C_k \), and the calculated reaction mixture component concentrations, \( \hat{C}_k \), i.e. by minimising the residual sum of squares \( S(\beta) \):

\[
S(\beta) = \sum_{k=1}^{v} \sum_{i=1}^{n_{\text{obs}}} \sigma^{kl} \left( C_{ki} - \hat{C}_{ki} \right)^2 \rightarrow \text{Min}
\]  

(4.1)

\( v \) being the number of responses, i.e. CHP, AC, PH, PP, AMS, DCP, DIM, BCAK and \( H_2O \), see Figure 4.3, \( n_{\text{obs}} \) being the number of experimental time sampling points and \( \sigma^{kl} \) being the \((k,l)\) elements of the inverse of the covariance matrix of the experimental errors on the responses \( C_k \). The latter was estimated from a preliminary parameter estimation based upon a minimisation of Equation 4.1 with \( \sigma^{kl} \) being the elements of the unity matrix, i.e. assuming equal variances for the errors of the different responses and neglecting any correlation. Minimisation was achieved with a multi-response Marquardt algorithm (Marquardt, 1963). The calculated product concentrations, \( \hat{C}_k \), were obtained by integration of the corresponding continuity equations:

\[
\frac{d\hat{C}_k}{dt} = R_{v,k} \quad k = 1, \ldots, v
\]  

(4.2)

with \( R_{v,k} \) the net rate of production of the corresponding component. The production rates follow from the law of mass action applied on the elementary steps. To facilitate the simultaneous estimation of the pre-exponential factors \( A_k \) and activation energies \( E_{\text{act},k} \), the following reparameterisation was applied on the reaction rate coefficients \( k_l \):
\[ k_i = A \exp\left(-\frac{E_{\text{act}i}}{RT}\right) = A^* \exp\left(-\frac{E_{\text{act}i}}{R}\left[\frac{1}{T} - \frac{1}{T_{av}}\right]\right) \quad (4.3) \]

\( T_{av} \) is the average temperature applied in the experiments, whereas the reparameterised pre-exponential factor \( A^* \) is defined by:

\[ A^* = A \exp\left(-\frac{E_{\text{act}i}}{RT_{av}}\right) \quad (4.4) \]

The significance of the individual parameter estimates is expressed as a calculated \( t \)-value, which is given by the ratio of the parameter estimate, \( b_i \), and the estimated standard error of the parameter estimate, \( s(b_i) \):

\[ t_i = \frac{b_i}{\sqrt{\text{variance}(b_i)}} = \frac{b_i}{s(b_i)} \quad (4.5) \]

These calculated \( t \)-values should be larger than 2 to indicate a parameter estimated significantly different from 0. With these \( t \)-values the \( 1-\alpha \) confidence intervals can be determined according to:

\[ b_i - t(n_{\text{obs}} - n_{\text{par}}, 1 - \frac{\alpha}{2})s(b_i) \leq \beta_i \leq b_i + t(n_{\text{obs}} - n_{\text{par}}, 1 - \frac{\alpha}{2})s(b_i) \quad (4.6) \]

with \( n_{\text{par}} \) the number of parameters. The significance of the global regression was expressed by means of the ratio of the mean regression sum of squares to the mean residual sum of squares, which is distributed according to the \( F \)-ratio (Draper and Smith, 1966):

\[ F - \text{ratio} = \frac{(n_{\text{obs}} - n_{\text{par}})\sum_{i=1}^{n_{\text{eq}}} [\hat{C}_i]^2}{n_{\text{par}}\sum_{i=1}^{n_{\text{eq}}} ([C_i] - [\hat{C}_i])^2} \quad (4.7) \]

A high value of the \( F \)-ratio corresponds to a high significance of the global regression over the whole range of investigated conditions. The adequacy of the mathematical models used for the regression was furthermore tested by analysis of residuals. Model discrimination was based on this adequacy, on the physical
The montmorillonite catalysed conversion of hydroperoxides

Figure 4.3 Network of observed global reactions.

meaning of the kinetic parameter estimates and on the statistical testing of the significance of the kinetic parameters and of the global regression.

4.3 Construction of the reaction network

4.3.1 Reactions with pure cumene hydroperoxide feed

The network of the observed global reactions is shown in Figure 4.3. Cumene hydroperoxide decomposes to acetone and phenol with a final selectivity approximating 100 %, see Figure 4.4.a. This reaction proceeds according to the

Figure 4.4.a Concentration vs. batch time during the decomposition of cumene hydroperoxide in cumene at 303 K with 0.5 kg m⁻³ F-20. b: Selectivity of BCAK vs. cumene hydroperoxide conversion for different initial cumene hydroperoxide concentrations. Symbols: experimental, curves: calculated with the parameter estimates reported in Table 4.IV.
The montmorillonite catalysed production of phenol and acetone from...

During decomposition of cumene hydroperoxide the origination of BCAK is observed, a component, which so far had not been reported in literature. The mechanism depicted in Figure 4.5 is proposed for its formation and is supposed to proceed by a mechanism analogous to the ketal formation, with hydroperoxides instead of alcohols. This mechanism starts with a nucleophilic addition of a cumene hydroperoxide molecule to an adsorbed and protonated acetone molecule, yielding the hemiketal. The hydroxy group of the hemiketal can be substituted by another hydroperoxide molecule, following a SN₁ mechanism. This way the side-product BCAK is obtained.

This mechanism explains the observations that upon formation of one molecule of BCAK also one molecule of water is formed and that one molecule of acetone and two molecules cumene hydroperoxide are consumed. The incorporation of acetone was deduced from differences between the acetone and phenol concentrations. Due

Figure 4.5 Structure and formation mechanism proposed for bis-cumylperoxy-acetone ketal (BCAK).
to the increase in the water concentration the reaction rate strongly decreased, as is generally the case with clay catalysed reactions (Mortland and Raman, 1968). Furthermore the homogeneous decomposition is also known to be sensitive to the water concentration (Cavaleri d'Oro et al., 1986; Burtzlaff et al., 1965; Jung and Just, 1971).

The initial selectivity towards BCAK of 0%, which is obtained by extrapolation of the selectivity vs. conversion curves to a conversion of 0%, see Figure 4.4.b, also indicates that a component, i.e. acetone, which is not present in the feed mixture, is involved in the formation of BCAK. Otherwise initial selectivities different from 0 would have been observed. The increase in the selectivity of BCAK vs. the cumene hydroperoxide concentration, see Figure 4.4.b, indicates that BCAK is formed with a rate proportional to a higher order in cumene hydroperoxide c.q. an order in acetone.
c.q. an order in water. This is in contrast to what is generally the case for SN1 reactions in which the rate is zero order with respect to the reactants. This deficiency may be explained by the occurrence of a more stable ionic intermediate in the mechanism. The data presented in fact show that this is the case. A reaction rate proportional to all components involved may take place if all reactions preceding the last shown in Figure 4.5 are in quasi-equilibrium.

Since BCAK disappears in the final stages of the reaction and always 100% selectivity towards the main products phenol and acetone was observed, BCAK also decomposes to these products. A mechanism analogous to the decomposition of the hydroperoxide is proposed, i.e. via a concerted mechanism in which the phenyl group migrates to the closest oxygen molecule, see Figure 4.6. This attack can be considered as an intramolecular SN2 substitution. During this attack the hemiketal is released, which can be dehydroxylated and attacked by another cumene hydroperoxide molecule as shown in Figure 4.5, or the hemiketal can also be subjected to the intramolecular phenyl attack and finally yield two acetone and one

Figure 0.7.a Concentration vs. batch time for cumene hydroperoxide (Co=125 mol m⁻³) mixed with 2-phenyl-2-propanol (Co=15 mol m⁻³) in cumene at 303 K with 0.5 kg m⁻³ F-20, b Concentration vs. batch time for 2-phenyl-2-propanol (Co=22 mol m⁻³) under same conditions. c Cumene hydroperoxide concentration vs. batch time with different initial 2-phenyl-2-propanol concentrations with 0.5 kg m⁻³ F-20 at 303 K in cumene. Symbols: experimental, curves: calculated with the parameter estimates reported in Table 4.1V.
phenol molecule, as illustrated in Figure 4.6. The reaction network presented in the upper half of Figure 4.3 now summarises the global reactions observed starting from pure hydroperoxide feed.

4.3.2 Reactions in the presence of typical feed stock components

The presence of the most abundant by-products of the oxidation of cumene affect the decomposition of cumene hydroperoxide to different degrees as will be outlined below.

**Acetophenone**

Acetophenone does not react nor influence the reactions that occur and therefore does not appear in the network in Figure 4.3. This observation is in agreement with the findings of previous studies with sulphuric acid as catalyst (Pritzkow and Hofmann, 1961).

**2-phenyl-2-propanol**

As pure feed 2-phenyl-2-propanol dehydrates to \( \alpha \)-methyl styrene, while mixed with cumene hydroperoxide, dicumyl peroxide is formed and hardly any \( \alpha \)-methyl styrene originates, see Figure 4.7.a and b. This indicates that the reaction of 2-phenyl-2-propanol with cumene hydroperoxide is faster than the dehydration of 2-phenyl-2-propanol. During both reactions water is formed, which decreases the catalyst activity. Hence, an increase in the 2-phenyl-2-propanol concentration leads to a decrease in the decomposition rate of cumene hydroperoxide, see Figure 4.7.c. This is again in agreement with earlier studies (Pritzkow and Hofmann, 1961; Fil'makova, 1974). Dicumyl peroxide, which is being formed in the presence of cumene hydroperoxide does not react further due to either a slower decomposition compared to cumene hydroperoxide, or due to the inhibiting effect of water, which is being formed in large amounts or due to competitive adsorption of reactants c.q. products present in the reaction mixture.

**Dicumyl peroxide**

Decomposition of dicumyl peroxide takes place at a longer time scale than the decomposition of cumene hydroperoxide and gives phenol, acetone, \( \alpha \)-methyl styrene and dimers as products, see Figure 4.8.b. During this decomposition no cumene hydroperoxide and 2-phenyl-2-propanol are observed, suggesting that these components are not formed as intermediates, or that the consecutive reactions to phenol and acetone and \( \alpha \)-methyl styrene and dimers are much faster than the preceding reactions to CHP and PP. When dicumyl peroxide and cumene hydroperoxide were treated simultaneously, cumene hydroperoxide decomposed to phenol and acetone as if no dicumyl peroxide was present. Dicumyl peroxide on the contrary hardly decomposed at all, see Figure 4.8.a. Possible explanations are the higher water concentrations during these experiments due to the higher humidity of
cumene hydroperoxide, or to competitive adsorption of the relative large amounts of cumene hydroperoxide, phenol c.q. acetone.

**α-methyl styrene**

The results of the experiments with α-methyl styrene are comparable to the results with dicumyl peroxide. As pure feed α-methyl styrene dimerises to 3 different isomers, while mixed with cumene hydroperoxide no reaction of α-methyl styrene takes place. The decomposition of cumene hydroperoxide is not affected by the presence of α-methyl styrene. The same explanations as given for the similar observations with dicumyl peroxide are applicable.

**Conclusion**

The presence of PP, DCP and AMS results in the occurrence of the reactions depicted in the lower half of Figure 4.3, which in total represents the network of all reactions observed during the production of phenol and acetone from industrial feed with F-20 as catalyst in cumene as solvent. Typical other impurities sometimes found during the sulphuric acid catalysed decomposition, like cumyl phenyl ether, cumyl phenols and mesityl oxide (Gerhartz et al., 1991; Cavalieri d'Oro, 1986) were not observed.

In Figure 4.9 a mechanism is proposed for the additional reactions occurring in the presence of PP, DCP and AMS. The phenyl-isopropyl cation (I') has a central place in this mechanism and is formed as an intermediate in most reactions. It can be formed by protonation of AMS, protonation and dehydration of PP and protonation of DCP followed by release of CHP as leaving group. Dicumyl peroxide may decompose via two potential routes. After protonation cumene hydroperoxide may be released, resulting in the formation of the central carbocation, which will deprotonate to α-methyl styrene. Also the intramolecular Sn2 mechanism, responsible for the decomposition of cumene hydroperoxide to phenol and acetone,
The montmorillonite catalysed conversion of hydroperoxides

Figure 4.9 Mechanism proposed for occurrence of reactions in presence of typical feed stock components other than the hydroperoxide. Numbers refer to reaction steps in the model shown in Table 4.111.

may take place, resulting in the release of 2-phenyl-2-propanol, and direct production of phenol and acetone. The experimental data could not distinguish between these routes, because both cumene hydroperoxide and 2-phenyl-2-propanol react much faster than the first step in the decomposition of dicumyl peroxide.

4.4 The effect of the montmorillonite type

The global kinetics of the main reaction were studied for several montmorillonites with varying acidity. To compare the results obtained, the disappearance of cumene hydroperoxide was assumed to be first order with respect to the hydroperoxide ($C_{CHP}$) and the catalyst concentration ($C_{cat}$):

$$- \frac{dC_{CHP}}{dt} = k_w C_{CHP} C_{cat} \quad (4.8)$$
The montmorillonite catalysed production of phenol and acetone from...

4.5 The effect of the process conditions

The factors affecting the kinetics of the cumene hydroperoxide decomposition, such as the temperature, the water concentration and the solvent type, were investigated in further detail and the results will be discussed in the following sub-paragraphs.

4.5.1 Temperature

The temperature was varied between 283 and 313 K, with cumene as solvent. The disappearance curves of cumene hydroperoxide in the temperature range of 283 - 303 K are shown as an example in Figure 4.11. Next to the influence on the reaction rates via the Arrhenius equation, the most pronounced effect of the temperature was...
observed on the selectivity of BCAK, see Figure 4.12. This selectivity decreases strongly as a function of temperature from a maximum of ±25% at 283 K to less than 5% at 303 K. This indicates that the activation energy for the formation of BCAK is much lower than the activation energy for the competing main reaction, or that the activation energy of its decomposition is very high. As a consequence, the decomposition carried out at lower temperatures leads to more inhibition by water. This is illustrated by the influence of the temperature on the disappearance curve of cumene hydroperoxide in Figure 4.11, which flattens more with time at lower temperatures as more BCAK is formed.

4.5.2 Water concentration

The important effect of the water concentration on the catalytic activity and hence the reaction rates has become qualitatively clear from the previous paragraphs. This effect is a general property of clay minerals and has been discussed extensively in the literature, see Chapter 3. The decomposition by mineral acids is furthermore also known to be affected by water (Burtzlaff et al., 1965; Jung and Just, 1971). If water is visualised as a weak base competing with the reactant for the protons, the effect can be described by the relation:

\[
\frac{1}{k} = a + bC_{H_2O}
\]  

(4.9)

with \( k \) being the pseudo-first order decomposition rate coefficient, and \( a \) and \( b \) the parameters of this equation determined by plotting \( 1/k \) vs. \( C_{H_2O} \). This relation has
occasionally been found for the mineral acid catalysed decomposition (Burtzlaff et al., 1965), but contradictory results were also observed (Jung and Just, 1971). During the decomposition catalysed by heteropolyacids, Kozhevnikov and Kulikov (1982), observed two regions; at $C_{H_2O} < 500 \text{ mol m}^{-3}$ Equation 4.9 appeared to be applicable, whereas at $C_{H_2O} > 500 \text{ mol m}^{-3}$ the reaction rate coefficient depended more strongly on $C_{H_2O}$: $k \sim C_{H_2O}^{-3}$.

To quantify the effect of the water concentration on the decomposition of cumene hydroperoxide by montmorillonites, the global reaction rate coefficient, see Equation 4.8, was determined at different water concentrations. Since cumene is a poor solvent for water, acetone was chosen as the solvent for these experiments. In acetone furthermore no BCAK was formed which would have complicated the kinetics due to the formation of additional water. This can be explained by a reduced acidity of F-20 in this solvent, see next sub-paragraph. The results are shown in Figure 4.13 and again clearly indicate the dramatic effect of the water concentration on the reaction rate.

The effect could not be described by the relations discussed above, but the reaction rate coefficient appeared to be related to $C_{H_2O}^{-1.76}$. In other words: via the introduction of a negative partial reaction order for water, the effect can be described very accurately:

$$-\frac{dC_{CHP}}{dt} = k_w C_{CHP} C_{cat} C_{H_2O}^{-1.76}$$

(4.10)

An explanation for this phenomenon is that the acid sites of the montmorillonite are very hydrophilic. Upon adsorption of each molecule of water, the acidity of the site

![Figure 4.13 Specific global reaction rate coefficient vs. water concentration for cumene hydroperoxide decomposition catalysed by F-20 at 323 K in acetone. Markers: experimental data points, curve: calculated by the equation depicted in the Figure.](image-url)
The montmorillonite catalysed conversion of hydroperoxides decreases due to dissipation of the proton charge over the extra water molecules (McCabe, 1992). The adsorption is reversible, which leads to a complex mixture of acid sites containing different amounts of adsorbed water, each with a different acid strength:

\[ \text{M}^{2+} + \text{aH}_2\text{O} \rightarrow \text{M(H}_2\text{O)}_{\text{a}}^{2+} \]  \hspace{1cm} (4.1)

in which \( \text{M}^{2+} \) represents a proton or strongly polarising cations like \( \text{Al}^{3+} \). The dependence of the activity on the amount of adsorbed water molecules is not known exactly, but the activity is known to decrease strongly with increasing amount of adsorbed water, as mentioned previously. Adsorption of more water therefore causes a decrease in the catalyst activity which cannot be described by a simple Langmuir-Hinshelwood equation, but can very well be described by the partial reaction order in water.

4.5.3 Solvent

Since the solvent type is also known to strongly affect the decomposition rate of cumene hydroperoxide in the mineral acid catalysed reaction, (Cavaliér d'Oro et al., 1986; Burtzlaff et al., 1965), its effect was also investigated for the montmorillonite catalysed decomposition. Figure 4.14 shows the results and clearly indicates that the decomposition is strongly favoured in apolar solvents such as heptane, toluene and cumene, over more polar solvents, such as acetone, ethyl acetate and ethanol. In the latter two solvents no reaction was observed at all. The more polar solvents apparently inhibit the decomposition. This may be caused by adsorption of the solvents on the acid sites, dissipating the proton charge and hence diminishing the acid strength.

![Figure 4.14](image_url)

**Figure 4.14** The effect of the solvent type on the specific pseudo first order reaction rate coefficient for the decomposition of cumene hydroperoxide by Filtrol F-20 at 313 K.
Although for the mineral acid catalysed decomposition no apolar solvents were investigated, the trend for the remaining solvents is identical, i.e. the same order: phenol/acetone > acetone > ethyl acetate > ethanol was found (Burtzlaff et al., 1965), although this effect was more pronounced for the mineral acid catalysed decomposition. The effect of phenol in the mineral acid catalysed decomposition was furthermore very extreme: an equimolar phenol/acetone mixture appeared to be 1000 times more active than acetone. This promoting effect of phenol was explained by Cavalieri d'Oro (1986) by an increase in the acid strength of the mineral acid. Zakoshanskii et al. (1986) developed a quantitative model for this phenomenon, based on the formation of phenol/acetone associates. Due to these associates less hydrogen bonding between the solvent and the mineral acid takes place, increasing the acid strength with two orders of magnitude. Although in the case of montmorillonites also an increase in the reaction rate was observed when an equimolar mixture of phenol/acetone was used instead of acetone, this increase only amounted to a factor 10 and may very well be attributed to the decreased polarity.

4.6 Modelling of the kinetics

Several models based on elementary reaction steps have been proposed in order to obtain more insight in the reaction mechanism and to determine which elementary reaction steps are kinetically significant. The kinetic parameters which are obtained by regression of the experimental data may furthermore be used for industrial reactor design purposes.

4.6.1 Model description

Discrimination between the models, which have been proposed and tested, was performed with the criteria outlined in paragraph 4.2.3. Furthermore as few steps as possible were incorporated to minimise the number of parameters to be estimated. This resulted in the model of elementary steps and reaction paths shown in Table 4.111. This model generally is a Langmuir-Hinshelwood mechanism, in which the reaction components compete for the active sites. The adsorptions, which can also be seen as protonations, are assumed to be in quasi-equilibrium and are taken independent of temperature. The catalyst is furthermore assumed to consist of uniform acid sites. For the intermediate $I^+$, see Figure 4.9, the pseudo-steady state approximation is applied. Therefore no absolute values, but ratios of the parameters $k_9$, $k_{10}$, $k_{12}$ and $k_{14}$ were obtained.

Steps 1 - 7 represent the reactions which occur in the absence of PP, DCP and AMS. The main reaction could simply be described by adsorption of CHP, followed by a reaction path directly leading to the products, i.e. except for competitive adsorption, the rate of the complete mechanism shown in Figure 2.17, is dependent only on the CHP concentration. This indicates that the reactions subsequent to the concerted intermediate all proceed very rapidly. The formation of BCAK could best
The montmorillonite catalysed conversion of hydroperoxides

Table 4.111 Elementary steps and reaction paths corresponding to considered global reactions

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction Path</th>
<th>Rate Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHP + H⁺ ⇄ CHP-H⁺</td>
<td>$\sigma_A \sigma_B \sigma_C \sigma_D \sigma_E \sigma_F$</td>
</tr>
<tr>
<td>2</td>
<td>CHP-H⁺ → AC⁺ + PH 1</td>
<td>0 0 0 0 0 0</td>
</tr>
<tr>
<td>3</td>
<td>AC + H⁺ ⇄ AC⁺</td>
<td>-1 -1 -1 -1 -1 -1</td>
</tr>
<tr>
<td>4</td>
<td>PH + H⁺ ⇄ PH⁺</td>
<td>0 0 0 0 0 0</td>
</tr>
<tr>
<td>5</td>
<td>AC⁺ + 2 CHP → BCAK-H⁺</td>
<td>-1 0 0 0 0</td>
</tr>
<tr>
<td>6</td>
<td>BCAK-H⁺ + H₂O → + H₂O</td>
<td>-1 0 0 0 0 0</td>
</tr>
<tr>
<td>7</td>
<td>BCAK + H⁺ ⇄ BCAK-H⁺</td>
<td>0 1 1 0 0 0</td>
</tr>
<tr>
<td>8</td>
<td>PP + H⁺ ⇄ PP⁺</td>
<td>0 0 0 1 0 0</td>
</tr>
<tr>
<td>9</td>
<td>PP⁺ + H₂ → I⁺ + H₂O</td>
<td>-1 1</td>
</tr>
<tr>
<td>10</td>
<td>I⁺ + CHP → DCP⁺</td>
<td>-1 -1 -1</td>
</tr>
<tr>
<td>11</td>
<td>DCP⁺ + H⁺ → DCP⁺⁺</td>
<td>0 0 0 1 0 0</td>
</tr>
<tr>
<td>12</td>
<td>I⁺ → AMS⁻</td>
<td>-1</td>
</tr>
<tr>
<td>13</td>
<td>AMS⁻ + H⁺ → AMS⁺</td>
<td>0 0 0 1 0 0</td>
</tr>
<tr>
<td>14</td>
<td>I⁺ + AMS → DIM⁺</td>
<td>-1</td>
</tr>
</tbody>
</table>

The decomposition of BCAK could be described by a simple first order reaction. Incorporation of the reverse of reaction 5 in the model shown in Table 4.111 did not improve the $F$- and $t$-ratios of the regression, indicating that the reverse of reaction 5 is not important.

The additional reactions occurring in the presence of PP, AMS and DCP are described by reaction steps 8 through 14 in Table 4.111, and are based on the mechanism depicted in Figure 4.9. The assumption that all steps except for step 14 are reversible, leads to the best regression result. The decomposition of DCP could theoretically be described by either mechanism shown in Figure 4.9, but model discrimination indicated that the reverse of step 10 is more probable than direct formation of phenol and acetone from DCP. Hence, although cumene hydroperoxide is formed in the reverse of step 10, its fast subsequent decomposition prevents that CHP is being observed experimentally. The dimerisation of AMS appeared to be irreversible as was already concluded experimentally, since nearly 100% conversion of AMS to its dimers was observed.

The most critical element in the tested models was the incorporation of the inhibition by water. The Langmuir-Hinshelwood model, in which acid sites on which water had been adsorbed are inactive could not adequately describe the experimental results. This was already expected from what is known about clay catalysis, because by adsorption of water the acid sites do not lose their activity completely, but the proton activity is decreased by dissipation of the cation charge (Adams et al., 1983). This was also found experimentally, see paragraph 4.5.2. Since the inhibition of the
montmorillonite by water in acetone could be described by introducing a partial reaction order \( n \) for water, this partial reaction order was also incorporated in the model by which the data of the experiments in cumene were regressed. The partial order was one of the parameters to be estimated and was incorporated in all acid catalysed steps, i.e. the products of the equilibrium constant with the corresponding reaction rate coefficients: \( K_1 \), \( k_2 \), \( K_3 \), \( K_7 \), \( k_6 \), \( K_8 \), \( k_9 \), \( K_{11} \), \( k_{10} \) and \( K_{13} \), \( k_{12} \), were all multiplied by \( C_{H_2O}^n \). The partial order was assumed to be equal for all steps.

### 4.6.2 Parameter estimates

The estimated parameters corresponding to the model discussed in the previous sub-paragraph are shown in Table 4.IV. They allowed an adequate description of all experimental data, which concern a broad range of process conditions, indicated by the parity diagrams in Figure 4.15. Examples of the adequacy can also be found in the graphs throughout this chapter.

Except for the activation energy of step -12, all parameters could be estimated significantly different from 0, indicated by their small 95% confidence intervals. The activation energy of step -12 therefore was set at 0 kJ mol\(^{-1}\), which isn't that unreasonable since it concerns in fact a protonation without any other rearrangements, and probably requires a much lower activation energy than the other reaction steps. The incorporation of the inhibiting effect of water by the introduction of a partial reaction order worked out very well. This was deduced from the F-ratio of this model, which was at least 2 times larger than the F-ratios of the Table 4.IV Parameter estimates with their individual 95% confidence intervals for the model as shown in Table 4.III and described in Paragraph 4.6.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( A^* )</th>
<th>Unit</th>
<th>( E_{act,i} )</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_2 ) ( K_1 )</td>
<td>( 3.3 \pm 0.3 \times 10^{-1} )</td>
<td>m(^3) kg(^{-1}) s(^{-1})</td>
<td>105 ± 4</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>( k_5 )</td>
<td>( 2.4 \pm 0.5 \times 10^{-1} )</td>
<td>m(^6) kg(^{-1}) mol(^{-1}) s(^{-1})</td>
<td>87 ± 10</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>( k_6 ) ( K_7 )</td>
<td>( 2.2 \pm 0.4 \times 10^{-1} )</td>
<td>m(^3) kg(^{-1}) s(^{-1})</td>
<td>266 ± 10</td>
<td></td>
</tr>
<tr>
<td>( k_9 )</td>
<td>( 1.4 \pm 0.3 \times 10^{-12} )</td>
<td>mol kg(^{-1}) s(^{-1})</td>
<td>109 ± 16</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>( k_{10} ) ( K_{11} )</td>
<td>( 2.3 \pm 0.2 \times 10^{-3} )</td>
<td>m(^3) kg(^{-1}) s(^{-1})</td>
<td>82 ± 6</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>( k_{12} ) ( K_{13} )</td>
<td>( 2.3 \pm 0.2 \times 10^{-3} )</td>
<td>m(^3) kg(^{-1}) s(^{-1})</td>
<td>0</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>( A^<em>/A_{12}^</em> )</td>
<td>-</td>
<td>-</td>
<td>-56 ± 19</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>( k_{10} )</td>
<td>( 3.2 \pm 0.6 \times 10^{-1} )</td>
<td>m(^3) mol(^{-1})</td>
<td>6 ± 19</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>( k_{14} )</td>
<td>( 2.8 \pm 0.4 \times 10^{-1} )</td>
<td>m(^3) mol(^{-1})</td>
<td>-44 ± 10</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>( K_3 )</td>
<td>( 8.0 \pm 1.0 \times 10^{-3} )</td>
<td>m(^3) mol(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_8 )</td>
<td>( 8.2 \pm 1.2 \times 10^{-3} )</td>
<td>m(^3) mol(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n )</td>
<td>( -2.44 \pm 0.05 )</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
models in which the water inhibition was incorporated by the Langmuir-Hinshelwood method or by the relations proposed by Burtzlaff et al. (1965) and Kozhevnikov and Kulikov (1982), see paragraph 4.5.2. The order in water turned out to be rather negative, i.e. -2.44 but its small 95% confidence interval shows that this parameter estimate is very reliable. The value is furthermore more negative than the value obtained in paragraph 4.5.2 for the decomposition in acetone. The lower polarity of cumene as solvent may increase the hydrophilic character of the montmorillonite, thereby increasing the adsorption of water on the surface and decreasing the acidity and activity of the catalyst at the same water concentrations.

The adsorption coefficients of CHP, PH, DCP, BCAK, AMS and the dimers could not be estimated significantly different from zero and they appeared to be highly correlated to other parameters. This indicates that these adsorptions are unimportant compared to the adsorption of AC and PP and hence, the fraction of free sites is not affected by the adsorption of the former group. As a consequence only values for $K_1 k_2$, $K_1 k_6$, $K_1 k_{10}$ and $K_1 k_{12}$ could be obtained, instead of for their separate values. From the estimated adsorption coefficients it can be concluded that PP adsorbs stronger than AC. The values indicate that during typical reaction conditions the fraction of free sites amounts to ±0.1.

The activation energy of the main reaction 2 amounted to 105 kJ mol$^{-1}$, which is higher than the apparent activation energy found for the homogeneous decomposition, which was determined at values ranging from 65 to 89 kJ mol$^{-1}$ (Pritzkow and Hofmann, 1961, Jung and Just, 1971, Fil'makova et al., 1974, Cavalieri d'Oro et al., 1986). The value of 105 kJ mol$^{-1}$ is comparable to the apparent activation energy from studies with another type of heterogeneous acids, the cation exchanger resins, which range from 86 to 114 kJ mol$^{-1}$ (Shelpakova et al., 1991; Vodnar, 1991). This indicates that for the reaction by heterogeneous catalysts a
higher activation energy is required, i.e. that the transition state in the reaction with heterogeneous acids consists of a higher energy.

The activation energy for the formation of BCAK was estimated at 87 kJ mol\(^{-1}\), whereas the decomposition of BCAK appeared to require a high activation energy of 266 kJ mol\(^{-1}\). This value seems unrealistically high, because the mechanism of the decomposition of BCAK is similar to the mechanism of the decomposition of CHP and therefore comparable activation energies are expected. Either the transition state of the decomposition of BCAK has a very high energy, or reaction steps 5 - 7 are a too simple representation of the actual reactions of the formation and disappearance of BCAK.

The estimated activation energies of \(k_9\), the dehydration of PP, and \(k_{10}\), the decomposition of DCP are also realistic with values of 109 and 82 kJ mol\(^{-1}\). The reparameterised pre-exponential factor of \(k_9\) is the highest, indicating that this step occurs with the highest frequency factor. As discussed previously only ratios of the parameters \(k_9, k_{10}, k_{12}\) and \(k_{14}\) could be determined. The reparameterised pre-exponential factors are within the same order of magnitude, indicating they all occur with comparable frequency factors. The activation energies differ somewhat more, with a difference of 62 kJ mol\(^{-1}\) between the highest and the lowest. The activation energy for \(k_{10}\), the formation of DCP is the highest, followed by \(k_{12}\) the formation of AMS, \(k_{14}\) the dimerisation of AMS and \(k_9\) the formation of PP.

### 4.7 Conclusions

The kinetics of the montmorillonite catalysed production of phenol and acetone from cumene hydroperoxide in the absence and presence of typical feed impurities have been investigated. The activity of dried Filtrol Grade F-20 is comparable to sulphuric acid and 100 % selectivity towards phenol and acetone is achieved. A so far unknown side product has been identified, which is suggested to be a ketal of acetone with two cumylperoxy groups. Water strongly inhibited all observed reactions. The presence of 2-phenyl-2-propanol leads to a decreased reaction rate due to an increase in the water concentration which is caused by reaction of 2-phenyl-2-propanol with cumene hydroperoxide to dicumyl peroxide and water. No dehydration of 2-phenyl-2-propanol to \(\alpha\)-methyl styrene is observed in the presence of cumene hydroperoxide. Acetophenone, dicumyl peroxide and \(\alpha\)-methyl styrene do not influence the decomposition of cumene hydroperoxide. The reactions of dicumyl peroxide and \(\alpha\)-methyl-styrene: decomposition to phenol, acetone, methyl styrene and dimers proceed at a longer time scale than the decomposition of cumene hydroperoxide and the dehydration of 2-phenyl-2-propanol.

It appeared that the strongly acidic montmorillonites are very active for the decomposition, while montmorillonites with moderate acid strength do not catalyse any reaction. Water has a very large negative effect on the activity of the
montmorillonite, which is more pronounced than found for the mineral acid catalysed decomposition. The more polar the solvent in which the reaction is carried out, the lower the decomposition rate. This may be attributed to stronger adsorption of the solvent, thereby decreasing both the availability and the acid strength of the catalytic sites.

A kinetic model is presented which could adequately describe the experimental data over a broad range of concentrations with a single set of physically reasonable parameter values. Kinetic parameters were obtained by regression of the data with the multi-response Marquardt algorithm. In this model the water inhibition was approximated by a negative order in water for the acid catalysed steps.

References

- Cavalieri d'Oro P., Perego C. and Raimondi L., 3rd World Congress on Chemical Engineering, Sept. 21-25, Tokyo, 1986.
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APPENDIX

VERIFICATION OF INTRINSICITY OF KINETICS

Intrinsic kinetic parameters can only be obtained if the reactions are carried out in the absence of diffusional limitations. Several relations, based on measurable quantities, have been developed in order to verify the absence of these limitations. This appendix demonstrates the absence of the different types of limitations for the montmorillonite catalysed conversion of cumene hydroperoxide as an example, but the same approach has been applied for hydroperoxyoctadecadienoic acid, see Chapters 7 and 8.

Criteria for neglecting diffusional limitations

Intraparticle diffusion limitation

To test whether the intraparticle diffusion rate is high enough to neglect the intraparticle concentration gradients, the effectiveness factor has to be calculated. This factor is higher than the required 0.95, if the weisz modulus, $\Phi$, is lower than 0.25:

$$\Phi = \frac{n + 1}{2} \frac{R_w^{obs} \rho_p (d_p / 6)^2}{D_e C_i} < 0.25$$  \hspace{1cm} (A.1)

where $n$ is the reaction order, $R_w$ the specific production rate, $\rho_p$ the density of the catalyst, $d_p$ the particle diameter, $D_e$ the effective intraparticle diffusion coefficient and $C_i$ the concentration of component $i$, for which the production rate was observed.
Intraparticle heat transport limitation

Intraparticle temperature gradients can be neglected when the following criterion is satisfied (Froment and Bischoff, 1990):

\[
\frac{(-\Delta H^0) r_{w}^{obs} d_p^{2} \rho_p}{\lambda_p T_s \frac{E_{act}}{RT_s}} < 3.0
\]  \hspace{1cm} (A.2)

in which \(\Delta H^0\) is the standard reaction enthalpy, \(E_{act}\) the activation energy, \(\lambda_p\) the heat conductivity of the catalyst particle, \(T\) the temperature and \(R\) the gas constant.

Mass transfer limitations

Mass transfer limitations can be neglected if the concentration difference between the bulk of the solvent \((C_{ib})\) and the outer surface of the catalyst particle \((C_{is})\) results in a difference in the reaction rate of less than 5%, for a partial reaction order of 1.5. This is the case if the following criterion is satisfied:

\[
\frac{R_{w}^{obs}}{d_p 6 k_{ij} C_{ib}} < 0.03
\]  \hspace{1cm} (A.3)

where \(k_{ij}\) is the mass transfer coefficient.

Heat transfer limitations

The criterion for neglecting heat transfer limitations is as follows (Froment and Bischoff, 1990):

\[
\frac{(-\Delta H^0) r_{w}^{obs} d_p \rho_p}{\alpha T_s \frac{E_{act}}{RT_s}} < 0.3
\]  \hspace{1cm} (A.4)

with \(\alpha\) the heat transfer coefficient.

Transport parameters

Molecular diffusion coefficient

The molecular binary diffusion coefficients were calculated using the relation of Scheibel (1954), which is a suitable relation for organic systems:

\[
D_{ij} = \frac{KT}{\eta_i \nu_j^{1/3}}
\]  \hspace{1cm} (A.5)
in which \( \eta \) is the viscosity of the solvent in cP \((=10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})\), \( V \) the molar volume in cm\(^3\) mol\(^{-1}\) of the dissolved component and \( K \) a coefficient with a value of 1.75 \(10^{-3}\).

The effective molecular diffusion coefficient can be calculated by:

\[
D_e = \frac{\varepsilon_p}{\tau_p} \frac{D}{4}
\]

(A.6)

in which \( \varepsilon_p \) is the porosity of the catalyst particle and \( \tau_p \) the tortuosity. Their ratio is roughly equal to \(1/4\).

**Mass transfer coefficient**

The mass transfer coefficient \( k_t \) can be calculated through the following equation:

\[
k_t = Sh \frac{D}{d_p}
\]

(A.7)

in which \( Sh \) represents the Sherwood number for which the following relation is applicable:

\[
Sh = 2 + 0.6 \text{ Re}^{1/2} \text{ Sc}^{1/3}
\]

(A.8)

where \( Re \) is the Reynolds number:

\[
Re = \frac{p_1 N d_m^2}{\eta_l}
\]

(A.9)

in which \( p_1 \) is the density of the liquid phase, \( N \) the number of revolutions of the mixer per second and \( d_m \) the diameter of the mixer. \( Sc \) represents the Schmidt number:

\[
Sc = \frac{\eta_l}{p_p D}
\]

(A.10)

**Heat transfer coefficient**

The mass transfer coefficient \( \alpha \) can be calculated through the following equation:

\[
\alpha = Nu \frac{\lambda_p}{d_p}
\]

(A.11)
The montmorillonite catalysed conversion of hydroperoxides

Table A.1 Conditions, properties of catalyst and liquid and calculated numbers and transport parameters according to relations described in this Appendix, for an example of a reaction of cumene hydroperoxide with F-20 in cumene.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Catalyst properties</th>
<th>Liquid properties</th>
<th>Numbers</th>
<th>Transfer coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{CHP,0}$</td>
<td>400 mol m$^{-3}$</td>
<td>$d_p$</td>
<td>$2 \times 10^5$ m</td>
<td>$\rho_l$</td>
</tr>
<tr>
<td>$T$</td>
<td>313 K</td>
<td>$\rho_p$</td>
<td>$5 \times 10^2$ kg$<em>{cat}$ m$</em>{cat}^{-3}$</td>
<td>$\eta_l$</td>
</tr>
<tr>
<td>$N$</td>
<td>15 s$^{-1}$</td>
<td>$\lambda_p$</td>
<td>1.0 J m$_{cat}^{-1}$ K$^{-1}$ s$^{-1}$</td>
<td>$\nu_{CHP}$</td>
</tr>
<tr>
<td>$d_m$</td>
<td>$1 \times 10^{-2}$ m</td>
<td>$\lambda_i$</td>
<td>$1.3 \times 10^{-1}$ J m$_{i}^{-1}$ K$^{-1}$ s$^{-1}$</td>
<td>$c_{p,l}$</td>
</tr>
<tr>
<td>Reaction properties</td>
<td></td>
<td></td>
<td></td>
<td>$D_i$</td>
</tr>
<tr>
<td>$-\Delta H_f^0$</td>
<td>$2.5 \times 10^5$ J mol$^{-1}$</td>
<td></td>
<td></td>
<td>$D_e$</td>
</tr>
<tr>
<td>$E_{act}$</td>
<td>$1.1 \times 10^5$ J mol$^{-1}$</td>
<td></td>
<td></td>
<td>$k_i$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Numbers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Re$</td>
<td>1980</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Sc$</td>
<td>380</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Sh$</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Pr$</td>
<td>8.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Nu$</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

in which $Nu$ represents the Nusselt number for which the following relation is applicable:

$$Nu = 2 + 0.6 \ Re^{1/2} Pr^{1/3}$$  \hfill (A.12)

$Pr$ is the Prandtl number analogous to the Schmidt number:

$$Pr = \frac{\eta_l c_{p,l}}{\lambda_l}$$  \hfill (A.13)

where $c_{p,l}$ is the specific heat and $\lambda_l$ the thermal conductivity of the liquid.

Verification of absence of diffusional limitations by an example.

Table A.1 summarises the data concerning the experimental conditions, the catalyst properties and the properties of the liquid, i.e. solvent and reactant, for an experiment in which cumene hydroperoxide with an initial concentration of 400 mol m$^{-3}$ is decomposed by 0.5 kg m$^{-3}$ F-20 at 313 K in cumene. This is the experiment with one of the highest production rates used for the modelling described in
Appendix

Verification of intrinsicity of kinetics

paragraph 4.6, and therefore the diffusional limitations are the most pronounced. Initially a production rate of cumene hydroperoxide of $-6.5 \text{ mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$ was observed under these conditions. This value and the values of the necessary parameters shown in Table A.1 are substituted in the criteria A.1 - A.4.

Intraparticle diffusion limitation

\[ \Phi = \frac{n+1}{2} \frac{P_{w}^{\text{obs}} \rho_{p} d_{p} / 6}{D_{o} C_{o,b}} = \frac{1+1}{2} \frac{16.5 \times 10^{-2} \left(2 \times 10^{-5} / 6\right)^{2}}{5 \times 10^{-10} 400} = 0.18 \quad (A.14) \]

This value calculated for the highest production rates, is close to the criterion limit of 0.25, indicating that diffusional limitations may play a minor role, especially if it is taken into account that several transport parameters are based on estimates. The activation energy determined by regression however appeared not to be affected by limitations, since the value is in the same order as literature values and in the case of limitations half the value would have been observed. The Weisz modulus for experiments carried out at lower temperatures was furthermore lower and hence no limitations are expected to exist under those conditions.

Intraparticle heat transport limitation

\[ \frac{(\alpha H^{0})_{r_{w}}^{\text{obs}} d_{p}^{2} P_{p}}{\lambda_{p} T_{s} R T_{s}} = \frac{2.5 \times 10^{5} 6.5 \left(2 \times 10^{-5}\right)^{2} 5 \times 10^{2} 1.1 \times 10^{5}}{1313 8.3 313} = 0.04 \quad (A.15) \]

Since this value clearly satisfies the criterion no intraparticle temperature gradients are present.

Mass transfer limitations

\[ \frac{P_{w}^{\text{obs}}}{6 k_{u} C_{o,b}} d_{p} = \frac{6.5 \times 2 \times 10^{-5}}{6 3.3 \times 10^{-3} 400} = 1.6 \times 10^{-5} \quad (A.16) \]

The criterion for mass transfer limitations also is convincingly satisfied and hence reactions take place without these limitations.

Heat transfer limitations

\[ \frac{(\alpha H^{0})_{r_{w}}^{\text{obs}} d_{p} P_{p}}{\alpha T_{s} R T_{s}} = \frac{2.5 \times 10^{5} 6.5 \times 2 \times 10^{-5} 5 \times 10^{2} 1.1 \times 10^{5}}{1.9 \times 10^{5} 313 8.3 313} = 0.01 \quad (A.17) \]
The value of 0.01 is thirty times as low as the criterion and hence no heat transfer limitations are expected to have occurred.

Conclusions

The example has shown that intraparticle diffusion limitations may have played a minor role for the experiments carried out at the highest temperature of 313 K. At lower temperatures however these limitations do not affect the intrinsic kinetics. The calculations have shown that the other types of diffusional limitations are not important.

References

5

EXPERIMENTAL AND ANALYTICAL PROCEDURES FOR THE CONVERSION OF HYDROPEROXYOCTADECADIEINOIC ACID

5.1 Introduction

The experiments presented in chapters 6 to 8 of this thesis, which describe the thermal and montmorillonite catalysed conversion of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid were all carried out batch wise. The reaction procedures and conditions and the procedures for the analysis of the reaction mixtures are described in paragraphs 5.2 and 5.3 respectively. The methods applied for the characterisation of the catalysts are outlined in paragraph 5.5. Due to the complexity of the reaction mixture much effort has been put in the identification and quantification of the major reaction products. This aspect will be discussed in paragraphs 5.6 and 5.7. Finally the definitions and calculations of the selectivities, yields and mass balances from the analysis results will be discussed in paragraph 5.8.

5.2 Production of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid

The reactant 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid (13-c,t-HPOD) was prepared by oxidation of linoleic acid, catalysed by the enzyme lipoxygenase extracted from soybeans. This procedure is based on the discovery by Hamberg (1971) who found that this enzyme selectively yields this hydroperoxide isomer. For the investigation described in this thesis, procedures were developed to produce larger quantities of this hydroperoxide isomer, resulting in two batches prepared by
The montmorillonite catalysed conversion of hydroperoxides

two different routes. Batch I was predominantly used for analytical purposes and explorative experiments while batch II was used for the mechanistic and kinetic studies described in chapters 6 - 8. Furthermore a mixture of all 4 HPOD isomers was prepared (batch III) for analytical purposes.

Batch I
Safflower oil, which contains 69 - 78% linoleic acid, was used as feed stock and was refined according to standard procedures: neutralisation with sodium hydroxide, bleaching with 0.5% Tonsil Standard FF (ex. Südchemie) and deodorisation. The oil, mixed with an equal amount of water, was hydrolysed to free fatty acids in an autoclave. The autoclave was operated at a temperature of 225 °C and a steam pressure of 35 bar and was flushed with 5 - 10 bar nitrogen. After 3 hours the reaction was stopped with a yield >95% and the water was removed under vacuum. The enzyme, necessary for the oxidation, was extracted from soy plates by dispersing 10 kg of soy plates in 90 kg of a 0.1 M acetate buffer (pH 4.5) and stirring at 4 °C for 3 hours. The debris was removed by centrifugation, leaving an enzyme solution of 820 µkatal l⁻¹. A batch reactor was flushed with pure oxygen and filled with 90 l of a 0.01 M potassium phosphate buffer (pH 9.5), containing 0.01% Tween 20, after which the oxygen flow was set at 10 l min⁻¹. 300 ml of the enzyme solution was added and subsequently the fatty acid mixture (255 g h⁻¹) and extra enzyme (3300 µkatal h⁻¹) were fed to the reactor. The pH was controlled by automatic addition of NaOH and foaming was controlled by automatic addition of Rhodorsil. At regular intervals samples were taken to determine the enzyme rest activity and hydroperoxide concentration. The process was stopped and cooled by addition of ice water when a: an increase in the enzyme rest activity, b: no further increase in the hydroperoxide concentration or c: an oil phase was observed. The mixture was brought at pH 4.5 by addition of 1 M HCl, centrifuged to remove the debris and extracted with petroleum ether. The petroleum ether was dried over sodium sulphate, filtered and evaporated. The raw hydroperoxide material with a purity of 30% (PV) was purified by column chromatography over silica with elution with hexane/diethyl ether.

Batch II
Linoleic acid (20 g, Sigma) was suspended in 1 l borate buffer (pH 9.1) and the mixture cooled to 0 °C with ice water. Lipoxidase 1B (2.5 mkatal, Sigma) was added to the well stirred solution and oxygen was bubbled through. The solution gradually became clear and the reaction was followed by thin layer chromatography (TLC) until no linoleic acid was left; the reaction was finished within 3 hours. The cold mixture was carefully acidified with 10% acetic acid to pH 5. The mixture was then extracted with diethyl ether, the ether layer was dried over magnesium sulphate, filtered and evaporated to leave 19 g of hydroperoxide, which left 1 spot on TLC.
Batch III
A 4% linoleic acid (99+%, Sigma) solution in MCT-oil was put away under air for 1 month. Under these conditions all four isomers are formed. This batch was used for analytical purposes, see paragraph 5.6.

5.3 Experimental procedure and reaction conditions
A Medium Chain Triglycerides oil (MCT-oil) was chosen as solvent, which served as an inert medium resembling a vegetable oil. MCT-oil is a triglyceride oil consisting of octanoic and decanoic acids as fatty acid groups, see Figure 5.1 and is in contrast to vegetable oils not oxidisable due to the absence of unsaturated fatty acid groups.

The inertia was necessary to exclude side reactions resulting from the presence of reactive unsaturated groups and focus on the reactions of the hydroperoxide. Except for this inertia, all other properties of MCT-oil are similar to vegetable oils. The MCT-oil was obtained from Bufa under the name Miglyol 812N and appeared to be very pure, i.e. components like mono- and diglycerides, phospholipids, free fatty acids, iron and other components, which could influence the experiments were present in negligible amounts, see Table 5.1. To avoid interference with the decomposition products of the hydroperoxide, the volatiles present in the MCT-oil were removed prior to use by an ultra high vacuum distillation technique.

Two types of experiments were performed. The hydroperoxide was either converted thermally or catalytically by an acid activated montmorillonite clay mineral. In both cases the reactions were performed in a thermostated batch reactor of 100 cm³. The range of reaction conditions applied in the experiments is shown in Table 5.11. Next to the MCT-oil as main solvent also other solvents were used: decane, toluene, cumene, ethyl octanoate and 1-butanol.
Table 5.11 Range of experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>Thermal</th>
<th>Catalytic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [K]</td>
<td>363 - 413</td>
<td>323 - 383</td>
</tr>
<tr>
<td>Main solvent</td>
<td>MCT-oil</td>
<td>MCT-oil</td>
</tr>
<tr>
<td>Batch time [ks]</td>
<td>0 - 500</td>
<td>0 - 100</td>
</tr>
<tr>
<td>$C_{HPOD,0}$ [mol m$^{-3}$]</td>
<td>30</td>
<td>7 - 60</td>
</tr>
<tr>
<td>Catalysts</td>
<td></td>
<td>Supreme FF, ACC FF,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>XJ-9126, F-20, B-80</td>
</tr>
<tr>
<td>$C_{cat}$ [kg m$^{-3}$]</td>
<td>-</td>
<td>2.5 - 10</td>
</tr>
<tr>
<td>$C_{H2O,0}$ [mol m$^{-3}$]</td>
<td>10 - 100</td>
<td>15 - 120</td>
</tr>
</tbody>
</table>

Thermal conversion
In a typical experiment the solvent and the hydroperoxide were added to the reactor in the required quantities and the reactor was brought under nitrogen by repeatedly switching between vacuum and nitrogen atmosphere. An initial sample was taken by a syringe punctured through a septum and subsequently the reactor was brought at the designated temperature, marking the start of the experiment. At suitable intervals samples were taken, which were rapidly cooled to stop the reactions. The samples were stored at -20 °C until they were subjected to analysis.

Montmorillonite catalysed conversion
The reactor with added solvent and hydroperoxide was brought under nitrogen at the designated temperature. After taking an initial sample, the catalyst was added while an overpressure of nitrogen was maintained to avoid the introduction of oxygen, marking the start of the experiment. At regular intervals samples were taken from which the catalyst was removed by pressing the sample through a syringe filter. The samples were stored at -20 °C until they were subjected to analysis. At the end of the experiment the catalyst was filtered off from the remaining suspension. The catalyst was washed thoroughly with hexane and dried at 90 °C under air for 2 hours. Supreme FF, which is a strongly acidic montmorillonite applied in the oil bleaching industry supplied by Südchemie, was used as main catalyst. The other

Table 5.111 Properties of montmorillonite catalysts used for conversion of HPOD.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Supplier</th>
<th>Acidity</th>
<th>Use</th>
<th>$A_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>$V_{pore}$ [cm$^3$ g$^{-1}$]</th>
<th>$d_{pore}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supreme FF</td>
<td>Südchemie</td>
<td>Strong</td>
<td>Bleaching</td>
<td>321</td>
<td>0.461</td>
<td>6.1</td>
</tr>
<tr>
<td>ACC FF</td>
<td>Südchemie</td>
<td>Medium</td>
<td>Bleaching</td>
<td>190</td>
<td>0.277</td>
<td>6.3</td>
</tr>
<tr>
<td>XJ-9126</td>
<td>Engelhard</td>
<td>Medium/Strong</td>
<td>Bleaching</td>
<td>314</td>
<td>0.444</td>
<td>6.0</td>
</tr>
<tr>
<td>F-20</td>
<td>Engelhard</td>
<td>Strong</td>
<td>General</td>
<td>286</td>
<td>0.335</td>
<td>5.4</td>
</tr>
<tr>
<td>B-80</td>
<td>Oil Dry</td>
<td>Weak/medium</td>
<td>Bleaching</td>
<td>137</td>
<td>0.278</td>
<td>13.3</td>
</tr>
</tbody>
</table>
types which have been used vary with respect to their acid strength, physical properties and typical application, see Table 5.111.

5.4 Analytical procedures

HPLC-UV analysis

HPLC separations were carried out with a set-up consisting of a TSP P200 pump, a TSP AS3000 autosampler and a TSP SpectraFOCUS rapid scanning UV-detector, see Figure 5.2. The MS was employed in rapid scanning mode (200 - 300 nm, 4 Hz) or in multiple wavelength mode (216, 235 and 270 nm). Data were sent via a TSP SpectraSystem SN4000 interface to a computer where the data could be manipulated with the TSP PC1000 software. A Lichrosorb Si-60 column (Merck, 250*4.6 mm) with 5 µm particles was used, eluted at 1.0 ml min⁻¹ with hexane/2-propanol/acetic acid (100/1/0.1 v/v/v). The samples were diluted by a factor 5 to 20 to appropriate concentrations with toluene, which appeared to be one of only a few solvents in which the samples were soluble and which did not affect the separation. 20 µl of the diluted samples were injected.

![Figure 5.2 HPLC-MS configuration](image)

HPLC-MS analysis

The HPLC with on-line MS studies were performed under the same HPLC conditions as described above. The postcolumn flow was first analysed by a multiple wavelength UV-detector operated at 235 and 270 nm. Mass spectra were subsequently obtained on a Fisons Trio2000 apparatus and were manipulated by MassLynx software. Several ionisation techniques were employed. On positive ElectroSpray (ES⁺) ionisation the postcolumn flow of 1 ml min⁻¹ was split in a ratio 1:50 and to the resulting 20 µl min⁻¹, 10 µl min⁻¹ of 0.1 mM sodium acetate in ethanol was added to enable the formation of (M + Na)⁺ adducts. A capillary voltage of 4.0 kV and a cone voltage of 50 - 55 V were applied at a temperature of 30 °C. Particle
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beam Electron Impact (EI) ionisation with an electron energy of 70 eV was incidentally used to obtain fragmentation patterns.

GPC-MS analysis
Gel Permeation Chromatography (GPC) was used to separate components differing in molecular size. The same configuration as with HPLC-MS was applied, with instead of the Lichrosorb column, one 500 Å and two 100 Å GPC columns (Polymer Laboratories, 5 µm particles, 7.5*300 mm) in series being used, eluted at 1 ml min⁻¹ with THF (Lichrosolv, Merck) as eluent. 100 µl of a sample, diluted with dichloromethane to an appropriate concentration was injected. The postcolumn flow was traced by UV, after which the larger part was split off. 10 - 15 µl min⁻¹ of 0.15 - 0.30 mM NaI in MeOH/EtOH (5/1 v/v) was added to the resulting flow (20 - 35 µl min⁻¹) to enable the formation of (M + Na)⁺ adducts during ES⁺-ionisation. The MS was employed with a capillary voltage of 4.2 kV and a cone voltage of 30 - 40 V at a temperature of 70 - 80 °C.

Direct MS
For direct MS, samples were diluted 50 to 100 fold with sodium iodide or sodium acetate dissolved in methanol/dichloromethane mixtures; which ratio depended on the sample. The samples were brought into the flow leading to the MS apparatus by means of a sixway valve, placed downstream of the splitter depicted in Figure 5.2. Direct MS was applied to tune the apparatus with a known substance in a solvent identical to the flow composition which is led into the MS during HPLC- or GPC-MS measurements or to screen reaction mixture samples for all mol masses present.

Peroxide Value (PV)
The peroxide value is a measure for the concentration of hydroperoxide groups and was determined according the Dutch NEN 6341. A known amount of sample was dissolved in 10 ml chloroform and 15 ml of glacial acetic acid was added. Subsequently 1 ml of a saturated sodium iodide solution was added and the mixture was shaken thoroughly after which the flask was put away for 5 minutes under the exclusion of light. The iodine formed was titrated with sodium thiosulfate against starch as indicator. The measurement was corrected by blank determinations. The PV is expressed as moles of active oxygen, i.e. hydroperoxide per m³. Pure linoleic acid hydroperoxide results in a PV of 3205 mol m⁻³. Other peroxides than hydroperoxides do not contribute to the PV.

Purge-and-trap analysis of hexanal
To determine the hexanal concentrations present in reaction mixtures a simple purge-and-trap analysis procedure was developed. 2 ml of a reaction sample was added to a vial, which was placed in a bath kept at 40 °C. In a closed system, the sample was purged during 2 hours with 80 ml min⁻¹ of nitrogen by a masterflex tubing pump. The nitrogen flow, containing evaporated volatiles was subsequently led through 2 ml of heptane placed in ice-salt bath of -15 °C where the volatiles were
trapped. This method was calibrated by purging known concentrations of hexanal in MCT-oil. Concentrations could be obtained with a measuring error of ca. 10%. The samples could not be subjected to temperatures higher than 40 °C, to avoid extra formation of volatiles during analysis. Due to this restriction only rather volatile products present in relatively high concentrations could be analysed, which practically meant that hexanal could be quantified by this method.

**Analysis of other volatile products**

A quantitative technique for the analysis of volatiles in oxidised oils was developed by Turksma (1992). In this technique samples are not subjected to temperatures higher than 30 °C and all volatiles are either quantitatively separated or the recoveries of the separation are well known. The procedure is not based on gas-liquid-solid equilibria as in many headspace techniques, which makes this method independent of the medium used or on the concentrations present. Due to the time-consuming procedure, experimental samples were only incidentally subjected to this method.

**Karl-Fischer water concentration analysis**

Water concentrations were determined by automatic Karl-Fischer coulometric titrations performed on a Metrohm 684 KF Coulometer, equipped with a 703 Titration unit, with Hydranal AG-H (Riedel-de Haen) as reagent.

### 5.5 Catalyst characterisation

The montmorillonite catalysts that were being used for the studies described in this thesis were characterised to determine the properties of the catalysts before and after reaction. In this way insight in the degree of deactivation of clay minerals was obtained. Suitable methods, which are furthermore applicable on a routine base are physisorption methods and elemental analysis.

**Particle diameter**

The average particle diameter of the catalysts was determined using a Coulter LS 130 apparatus, operated with a laser source of 750 nm. From the diffraction pattern the average particle diameter was calculated, assuming spherical particles.

**Physisorption measurements**

Adsorption isotherms of the catalysts were measured on the ASAP2010 apparatus of Micromeritics at 77 K with nitrogen as adsorbent. The catalysts were dried for 30 mins at 363 K under a pressure of 10 Pa before their isotherms were measured. The specific surface areas were calculated with the Brunauer, Emmet and Teller (BET) theory. Total pore volumes were determined from single point calculations. Pore size distributions, from which the average pore diameter sizes could be determined, were calculated from the adsorption isotherm, using the Barrett, Johner and Halenda (BJH) theory.
In Table 5.11 the physical properties as determined by the physisorption measurements are reported for the fresh catalysts which have been used for the conversion of 13-c,t-HPOD. Supreme FF and XJ-9126 are the types with the highest BET surface areas, followed by F-20, which has somewhat smaller pores and as a consequence a lower pore volume. ACC FF contains a lower BET surface area with comparable pore size as the former two, while B-80 has an even smaller surface area but relatively very large pores.

Elemental analysis

A standard method was applied to determine the carbon, hydrogen and oxygen content of the catalysts. The carbon content is a measure for the amount of organic material, "coke", deposited on the catalyst.

5.6 Identification of reaction products

5.6.1 Introduction

In the past decades many identification techniques have been applied to elucidate the complex mixture of components resulting from the oxidation of fatty acids and/or the decomposition of their hydroperoxides. Volatile products are relatively easy identified by GC-MS of headspace samples (Grosch, 1987). Quantitative information about the volatile concentrations however is less readily obtained since under the analysis conditions easily extra volatiles are formed. GC-MS can also be used for the identification of less volatile components if derivatisations are applied, like hydrogenation, esterification or trisilylation (Terao et al., 1974; Frankel et al., 1977). Disadvantages however are that no distinction can be made between hydroperoxy and hydroxy groups and between saturated and unsaturated components and that high temperatures are employed which may decompose other unstable components present, like peroxides, not susceptible to the derivatisation. Other techniques consist of preparative separation of different components by HPLC or TLC, followed by identification with NMR or MS (Schieberle and Grosch, 1981a; Frankel et al., 1982). The components again often are derivatised to increase the volatility and the susceptibility towards ionisation. These procedures however are very time consuming and require specific expertise. The studies towards identification of oligomeric components are even more complicated. The papers of Miyashita et al. (1982a,b, 1984, 1985), describing multiple step separations using various chromatographic techniques are the most elucidating in this field of research.

For the identification of the reaction products resulting from the thermal and montmorillonite catalysed conversion of 13-c,t-HPOD described in this thesis, a new procedure was applied. By HPLC with UV detection a separation of the UV-sensitive reaction products was developed, which resulted in the application as described in the previous paragraph. The same HPLC conditions were used for the HPLC-MS technique to identify these reaction products. ElectroSpray ionisation was used as
the main ionisation technique. This ionisation technique has only been available commercially since a few years and is especially suitable for thermally less stable and more polar components, such as peptides and proteins. The ionisation technique is very soft, which means that it does not fragment the molecule, giving direct information about the mol mass. Since this method has recently been applied successfully for the determination of mol masses of triglycerides, the idea originated that this method could also be applied for the identification of linoleic acid hydroperoxide reaction products. Ions would be generated by the addition of a (small amount of) sodium or ammonium salt to the sample or post column flow, resulting in the pseudomolecular \((M+Na)^+\) or \((M+NH_4)^+\) ions generally obtained. A polar solvent such as methanol or ethanol has to be added to the apolar postcolumn flow, mainly consisting of hexane, to enable the formation of these ions.

Before the reaction samples were subjected to HPLC-MS, the apparatus was tuned with linoleic acid, directly injected, as probe molecule. Sodium acetate was used as the salt to generate the ions. The mass spectrum obtained is shown in Figure 5.3. From this Figure it is clear that hardly any of the expected \((M+Na)^+\) ions are formed, and that the \((M-H+2Na)^+\) ions are the most dominant. The mass spectrum is furthermore complicated by the formation of acetate clusters. This phenomenon is probably due to the relative low polarity of the solvent used for this analysis, leading to aggregation of the ionic species with extra acetate and sodium ions. The \(M/Z^+\) of 407 for example is derived from \((M-H+2Na+NaOAc)^+\). The origin of the other ions is shown in Table 5.1V. With this knowledge the mass spectra of the components eluting from the HPLC were interpreted. Identification was based on combined data from the mass spectra, UV-spectra, elution order and reactivity of the hydroperoxdiene group. For identification purposes, samples from the feed mixture and from reaction mixtures were analysed. A summary of all data obtained is shown in Table 5.VI. The structures of the identified components are depicted in Figure 5.8.

![Figure 5.3 ES+MS spectrum of linoleic acid.](image-url)
5.6.2 Assignment of components by analysis of the feed mixture.

Hydroperoxyoctadecadienoic acids
In Figure 5.4, the HPLC-chromatogram as analysed by UV-detection at 235 nm is shown for the hydroperoxide from batch II, prepared by enzymatic oxidation described in par. 5.2, and for the hydroperoxide from batch III resulting from aerobic oxidation of linoleic acid. In the enzymatic prepared sample one isomer dominates, assigned to 13-c,t-HPOD, which is the expected isomer (Hamberg, 1971). In the aerobic oxidised sample 4 isomers appear, which are the 9- and 13- and cis,trans- and trans,trans- isomers of hydroperoxy octadecadienoic acid (Chan and Levett, 1977; Schieberle and Grosch, 1981b). The first isomer to elute has the same retention time and UV-spectrum as the hydroperoxide derived from enzymatic oxidation, indicating the same isomeric composition. Since it is known that the positional 9- and 13-cis,trans- isomers are formed in the

<table>
<thead>
<tr>
<th>M/Z+</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>317</td>
<td>(M+Na-H2O)+</td>
</tr>
<tr>
<td>335</td>
<td>(M+Na)+</td>
</tr>
<tr>
<td>339</td>
<td>(M-H+2Na-H2O)+</td>
</tr>
<tr>
<td>357</td>
<td>(M-H+2Na)+</td>
</tr>
<tr>
<td>461</td>
<td>(M-2H+3Na+NaOAc)+</td>
</tr>
<tr>
<td>625</td>
<td>(M-2H+3Na+3NaOAc)+</td>
</tr>
<tr>
<td>669</td>
<td>(2M-H+2Na)+</td>
</tr>
</tbody>
</table>

Figure 5.5 ES+-MS spectrum of 13-c,t-HPOD

Table 5.V Origin of ions from ES+-ionisation of HPOD separated by HPLC.
same amount (Frankel *et al.*, 1977), and it is observed that the first and third peak have the same peak area, the third eluting isomer is attributed to 9-hydroperoxy-10-trans,12-cis-octadecadienoic acid (9-c,t-HPOD). The second and fourth eluting isomer are attributed to 13-hydroperoxy-9-trans,11-trans-octadecadienoic acid (13-t,t-HPOD) and 9-hydroperoxy-10-trans,12-trans-octadecadienoic acid (9-t,t-HPOD), assuming that the 13-isomer elutes before the 9-isomer as in the case of the cis,trans-isomers. The trans,trans-isomers displayed a maximum in the UV-absorptivity at somewhat lower wavelength than the cis,trans-isomers: 229 vs. 233 nm. This is confirmed by the data of Chan and Levett (1977). The ES+ mass spectra of the isomers were identical and the dominant M/Z+ ions can easily be explained by the formation of the same type of adducts as the observed with linoleic acid, see Figure 5.5 and Table 5.V. The formation of M/Z+ 247 may, despite the soft ionisation technique, have originated from fragmentation of the hydroperoxide to 13-oxo-9,11-tridecadienoic acid. The latter is also formed during thermal treatment of the hydroperoxide, as will be shown later this paragraph.

**Hydroxyoctadecadienoic acids**

The hydroxyoctadecadienoic acid (HOD) isomers were assigned according the same procedure applied for the hydroperoxy components, after reduction of the hydroperoxide samples with triphenylphosphine (TPP). TPP is known to quantitatively reduce hydroperoxides to hydroxides with retention of the isomeric composition (Denney *et al.*, 1959; Nakamura and Maeda, 1991). The HPLC-chromatogram of the hydroxy-isomers obtained by reduction of the hydroperoxy sample, prepared by aerobic oxidation of linoleic acid is shown in Figure 5.6. The assignment in order of elution is 13-hydroxy-9-cis,11-trans- (13-c,t-HOD), 13-hydroxy-9-trans,11-trans- (13-t,t-HOD), 9-hydroxy-10-trans,12-cis- and 9-hydroxy-10-trans,12-trans-octadecadienoic acid (9-t,t-HOD). The data summarising the identification are shown in Table 5.VI.

5.6.3 Assignment of components by analysis of reaction mixtures

In Figure 5.7, typical chromatograms of reaction samples from treatment of 13-c,t-HPOD either with Supreme FF or thermally are shown. The chromatograms are obtained by UV-absorption at 235 and 270 nm and as total ion chromatogram (TIC),
obtained by ES+ ionisation. In these chromatograms the hydroperoxide isomers, identified in the previous paragraph are numbered 13, 16, 18 and 19, while the numbers 12, 20, 21 and 22 refer to the hydroxy isomers.

In the thermally treated sample furthermore components were detected with mol masses corresponding to diglycerides with C₈ and C₁₀ fatty acids, denoted by D in

Figure 5.7 HPLC chromatograms of a montmorillonite treated and b thermally treated 13-c, t-HPOD with 1 MS-detection, 2 UV 235 nm detection and 3 UV 270 nm detection.
the TIC-chromatograms. These diglycerides are probably formed by partly hydrolysis of the MCT triglycerides. Although it goes beyond the scope of this thesis it is interesting to note that the analysis applied is able to separate 6 different diglycerides containing C₈ and C₁₀ fatty acids.

2,4-decadienal (DD)
After the solvent the first component to elute, designated 1, had an UV-maximum of 263 nm, indicative of a triple conjugated system. No ES+-mass spectrum could be obtained for this component, due to the relatively high volatility, which makes decadienal disappear together with eluent. The retention time (6.23 min), however, exactly coincided with that of commercially obtained 2,4-decadienal, which also had the same UV-spectrum. These data strongly indicate that the component is decadienal. No distinction could be made between the cis,trans- and the trans,trans-form.

Octadecatrienoic acid (OT)
The second component had a more complex UV-spectrum with the main maximum at 268 nm, another maximum at 278 nm and a shoulder at 257 nm. This spectrum is typical of a triene structure. The mass spectrum suggests a mol mass of 278 by the presence of M/Z⁺-ions of 301 (M+Na)+, 323 (M-H+2Na)+ and 487 (M-H+2Na+2NaOAc)+. Combination of this information leads to the conclusion that this component is octadecatrienoic acid (OT). With 13-c,t-HPOO as reactant the triene structure is positioned at 9,11,13 or 8,10,12 and either in the cis,trans,trans- or in the trans,trans,trans-form.

Oxooctadecadienoic acids (OOD)
Components 6, 8 and 10 all displayed the same ES+-mass spectrum, with the M/Z⁺-ions 317 (M+Na)+, 339 (M-H+2Na)+, 421 (M-H+2Na+NaOAc)+ and 503 (M-H+2Na+2NaOAc)+ being the most dominant, indicating a mol mass of 294. Components 6, 8 and 10 showed UV-maxima of 272, 267 and 267 nm respectively, all indicating a triple conjugated system. Based on these data, it was concluded that these components are isomers of a conjugated oxooctadecadienoic acid (OOD). Since component 6 was already present to a minor degree in the start sample, this component is probably directly derived from 13-c,t-HPOO and has therefore the same isomeric stereo configuration : 13-oxo-9-cis,11-trans-octadecadienoic acid (13-c,t-000). The fact that components 8 and 10 show a lower UV-maximum suggests that these components are in the trans,trans-form, similar to the situation described for the hydroperoxy- and hydroxy-isomers. Because component 8 elutes before component 10, components 8 and 10 are. identified respectively as 13-oxo-9-trans,11-trans- (13-t,t-OOD) and 9-oxo-10-trans,12-trans-octadecadienoic acid (9-t,t-OOD). The 13-isomers of the hydroperoxy and hydroxy components, namely, also eluted before the 9-isomers. In the experiment in which linoleic acid was oxidised under aerobic conditions, the OOD isomers were formed as by-products. It appeared that the peak area of component 8 was equal to the added peak areas of
The montmorillonite catalysed conversion of hydroperoxides

components 6 and 10. Since 4 isomers are expected and the 9-oxo-10-trans,12-cis-isomer (9-c,t-OOD) has not been subscribed to a peak it is concluded that component 8 is in fact an unseparable mixture of the 9-c,t-OOD and 13-t,t-OOD. The latter is usually formed in much larger amounts as is the case in the chromatograms depicted in Figure 5.7, indicated by the UV-spectrum in which the trans,trans-form dominates.

12-oxo-10-trans-dodecenoic acid (ODE)
Component 15, which is formed only during the montmorillonite catalysed conversion, appeared to have an UV-maximum of 215 nm, indicative of a vicinal oxoene function. The ES+mass spectrum was dominated by the M/Z+ -ions 235 (M+Na)+ and 257 (M-H+2Na)+, suggesting a mol mass of 212. Based on these data and the known acid catalysed Hock-cleavage for hydroperoxides, see paragraph 2.5, this component is identified as 12-oxo-10-trans-dodecenoic acid (ODE). The UV-absorbency maximum is confirmed by literature (Makin et al., 1974).

13-oxo-9,11-tridecadienoic acids (OTD)
Peaks 14 and 17 predominantly originate during thermal treatment of the hydroperoxide and show a maximum UV-absorbency of resp. 268 and 264 nm. This again suggests the presence of a triple conjugated system. The mass spectra of these components are identical and show the M/Z+ -ions of 247 (M+Na)+ and 269 (M-H+2Na)+ as main ions, indicating a mol mass of 224. Identification of these products as 13-oxo-9,11-tridecadienoic acid (OTD) meets all the requirements. Component 14 most probably is the cis,trans form (13-c,t-OTD) and component 17 the trans,trans-form (13-t,t-OTD), deduced from the elution order and assuming that this order is dependent in the same way for these components as for the components described above. The higher UV-absorbency maximum observed for 13-c,t-OTD compared to 13-t,t-OTD also is in line with the observations for the other components for which for the cis,trans-isomers higher UV absorbency maxima were found. It is furthermore known that the trans,trans-form is more stable. The fact that component 17 appeared to be more stable under severe conditions confirms this assumption.

Components U1, U2, U3 and U4
Components 3, 4, 5 and 7, which are formed exclusively during the montmorillonite catalysed conversion of the hydroperoxide, could not be identified completely. While component 3 displays a maximum in the UV-absorbency at 274 nm, the other components display a maximum around 230 nm: resp. 234, 230 and 230 nm. This indicates that component 3 is triple conjugated and the other components are double conjugated. The ES+mass spectra of the four components are identical to each other and to the mass spectra of OOD, suggesting that these 4 components all have a mol mass of 294. Component 3 could be another isomer of a triple conjugated oxooctadecadienoic acid, but the exact structure is not that obvious, even when known reaction products from literature are considered. Components 4, 5
and 7 could also be oxooctadecadienoic acids, with only two of the three unsaturations conjugated. Another possible identity is a double conjugated epoxide. In this thesis components 4, 5, 7 and 3 are referred to as U1, U2, U3 and U4.

![Diagram of chemical structures](image)

**Figure 5.8** List of identified components, analysed on routine basis. Numbers refer to peak numbers assigned to components in Figure 5.7.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid</td>
<td>13-c,t-HPOD</td>
<td>21.7</td>
<td>233</td>
<td>247, 335, 357, 461</td>
<td>312</td>
<td>26000^a</td>
</tr>
<tr>
<td>• 13-hydroperoxy-9-trans,11-trans-octadecadienoic acid</td>
<td>13-t,t-HPOD</td>
<td>25.8</td>
<td>230</td>
<td>247, 335, 357, 461</td>
<td>312</td>
<td>28600^a</td>
</tr>
<tr>
<td>• 9-hydroperoxy-10-trans,12-cis-octadecadienoic acid</td>
<td>9-c,t-HPOD</td>
<td>31.3</td>
<td>233</td>
<td>247, 335, 357, 461</td>
<td>312</td>
<td>25900^a</td>
</tr>
<tr>
<td>• 9-hydroperoxy-10-trans,12-trans-octadecadienoic acid</td>
<td>9-t,t-HPOD</td>
<td>32.3</td>
<td>230</td>
<td>247, 335, 357, 461</td>
<td>312</td>
<td>28600^a</td>
</tr>
<tr>
<td>• 13-hydroxy-9-cis,11-trans-octadecadienoic acid</td>
<td>13-c,t-HOD</td>
<td>19.3</td>
<td>232</td>
<td>319, 341, 423, 505</td>
<td>296</td>
<td>27200^a</td>
</tr>
<tr>
<td>• 13-hydroxy-9-trans,11-trans-octadecadienoic acid</td>
<td>13-t,t-HOD</td>
<td>34.2</td>
<td>229</td>
<td>319, 341, 423, 505</td>
<td>296</td>
<td>30500^a</td>
</tr>
<tr>
<td>• 9-hydroxy-10-trans,11-cis-octadecadienoic acid</td>
<td>9-c,t-HOD</td>
<td>43.2</td>
<td>233</td>
<td>319, 341, 423, 505</td>
<td>296</td>
<td>28300^a</td>
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<td>9-t,t-HOD</td>
<td>48.8</td>
<td>229</td>
<td>319, 341, 423, 505</td>
<td>296</td>
<td>31600^a</td>
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<tr>
<td>• 13-oxo-9-cis,11-trans-octadecadienoic acid</td>
<td>13-c,t-OOD</td>
<td>11.6</td>
<td>272</td>
<td>317, 339, 421, 503</td>
<td>294</td>
<td>20900^b</td>
</tr>
<tr>
<td>• 13-oxo-9-trans,11-trans-octadecadienoic acid</td>
<td>13-t,t-OOD</td>
<td>13.3</td>
<td>267</td>
<td>317, 339, 421, 503</td>
<td>294</td>
<td>20900^b</td>
</tr>
<tr>
<td>• 9-oxo-10-trans,11-cis-octadecadienoic acid</td>
<td>9-c,t-OOD</td>
<td>13.3</td>
<td>?</td>
<td>317, 339, 421, 503</td>
<td>294</td>
<td>20900^b</td>
</tr>
<tr>
<td>• 9-oxo-10-trans,12-trans-octadecadienoic acid</td>
<td>9-t,t-OOD</td>
<td>14.4</td>
<td>267</td>
<td>317, 339, 421, 503</td>
<td>294</td>
<td>20900^b</td>
</tr>
<tr>
<td>• 9,11,13-8,10,12-cis/trans,trans,trans-octadecatrienoic acid</td>
<td>OT</td>
<td>6.2</td>
<td>268, 278, 257</td>
<td>301, 323</td>
<td>278</td>
<td>56000^c</td>
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<tr>
<td>• 13-oxo-9-cis,11-trans-tridecadienoic acid</td>
<td>13-c,t-OTD</td>
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<td>268</td>
<td>247, 269</td>
<td>224</td>
<td>30000^d</td>
</tr>
<tr>
<td>• 13-oxo-9-trans,11-trans-tridecadienoic acid</td>
<td>13-t,t-OTD</td>
<td>30.0</td>
<td>264</td>
<td>247, 269</td>
<td>224</td>
<td>30000^d</td>
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<tr>
<td>• 12-oxo-10-trans-dodecenoic acid</td>
<td>ODE</td>
<td>24.7</td>
<td>215</td>
<td>235, 257</td>
<td>212</td>
<td>15500^d</td>
</tr>
<tr>
<td>• 2-trans,4-cis/trans-decadienal</td>
<td>DD</td>
<td>5.5</td>
<td>263</td>
<td></td>
<td>212</td>
<td>30000^d</td>
</tr>
<tr>
<td>• Unknown1</td>
<td>U1</td>
<td>10.0</td>
<td>234</td>
<td>317, 339, 421, 503</td>
<td>294</td>
<td>26000^e</td>
</tr>
<tr>
<td>• Unknown2</td>
<td>U2</td>
<td>10.8</td>
<td>230</td>
<td>317, 339, 421, 503</td>
<td>294</td>
<td>26000^e</td>
</tr>
<tr>
<td>• Unknown3</td>
<td>U3</td>
<td>12.6</td>
<td>230</td>
<td>317, 339, 421, 503</td>
<td>294</td>
<td>26000^e</td>
</tr>
<tr>
<td>• Unknown4</td>
<td>U4</td>
<td>8.8</td>
<td>274</td>
<td>317, 339, 421, 503</td>
<td>294</td>
<td>21000^e</td>
</tr>
</tbody>
</table>

Chapter 5  
Experimental and analytical procedures for the conversion of hydroperoxy...

Figure 5.9 GPC-MS chromatograms of feed mixtures. a batch I, b batch II.

5.6.4 GPC-MS analysis for identification of oligomers

The analyses described in the previous paragraph did not reveal any oligomeric material as reaction products, although many literature data indicate that these components are major products (Frankel et al., 1960). Since these oligomeric components may coincide with the solvent in the HPLC-chromatogram, a GPC-MS analysis was developed to separate the samples based on molecular size. The fact that this application uses a rather polar eluent, THF, furthermore simplified the mass spectra in such a way that only the \((\text{M+Na})^+\) were formed during ES+-ionisation.

Table 5.VII Most abundant mol masses in GPC-fractions.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Most abundant mol masses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900, 902, 920, 918, 934, 884, 886, 870</td>
</tr>
<tr>
<td>2</td>
<td>606, 608, 590, 588, 624, 576, 574, 640</td>
</tr>
<tr>
<td>3a</td>
<td>412, 410, 312, 428, 328</td>
</tr>
<tr>
<td>3</td>
<td>294, 296, 312</td>
</tr>
<tr>
<td>4</td>
<td>294</td>
</tr>
</tbody>
</table>

In Figure 5.9, GPC-chromatograms of the feed mixtures are shown, detected as total ion chromatogram. It is clear that batch I contains a mixture of components varying in molecular size. Fraction 1 consists of trimers, 2 of dimers and 3 and 4 of monomers. Fraction 3a contained mol masses between dimeric and monomeric components. The most abundant mol masses are shown in Table 5.VII. It appeared that the monomeric fraction 4 mainly consisted of OOD. Structures proposed for several of the main dimeric masses are depicted in Figure 5.10. These dimers can be formed by radical induced reactions between hydroperoxy (and hydroxy- or oxo-) components as described in paragraph 2.4.4. Batch II appeared to be much purer as indicated by the fact that only monomeric fractions are present with the M/Z of 335 \((\text{HPOD+Na})^+\) as dominant ion, next to smaller amounts of oxooctadecadienoic acid in fraction 4.
When the hydroperoxide from batch I was treated either thermally or with montmorillonites, the amount of dimers or trimers did not change significantly. The oligomeric mol masses detected in the treated samples were globally the same as in the feed mixture, although the ratio in which they were present shifted to components with lower mol masses. During the montmorillonite treatment the oligomers with mol masses of 886, 902, 920, 590, 608 and 576 completely disappeared. During treatment, especially with montmorillonites, furthermore components with mol masses of 1½ and 2½ times the monomer mol mass originated, indicating cleavage of dimers and trimers or addition of a cleaved molecule to a monomer or dimer.

5.7 Quantification of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid reaction mixture

The identified components, listed in Figure 5.8, were quantified by the following procedure. The total initial concentration of the 4 HPOD isomers in batch II was assumed to be equal to the PV, i.e. it was assumed that no other hydroperoxides than HPOD were present:

\[
C_{\text{HPOD,tot,0}} = PV_0
\]  

This assumption can be made based on the high purity of the feed mixture as indicated by HPLC and GPC measurements. The concentration of the individual hydroperoxide isomers \(C_{\text{HPOD,i,o}}\) during reaction was determined by relating their peak area \(PA_{\text{HPOD,i,t}}\) in the HPLC-UV (235 nm) chromatogram to the total peak area of the HPOD isomers in the feed mixture \(PA_{\text{HPOD,tot,0}}\), correcting for differences between their molar absorbancies, which were obtained from Chan et al. (1979).
The relative molar absorbancies of the components were used to calculate the concentrations of the other components in the reaction mixtures. The concentration of component X is determined by:

\[
C_{X,t} = P_{A,t} \frac{\varepsilon_{HPOD}}{\varepsilon_X} \frac{C_{HPOD, tot,0}}{P_{A, HPOD, tot,0}}
\]  

These molar absorbancies, see Table 5.VI, were taken from literature with the molar absorbancy of the 13-oxo-9,11-tridecadienoic acids (OTD) assumed to be equal to the molar absorbancy of 2,4-decadienal (DD) and the molar absorbancy of 12-oxo-10-dodecenoic acid (ODE) assumed to be equal to that of 2-dodecenal. These assumptions can be made because these components contain the same type of conjugation. For the quantification of components U1 - U3 an molar absorbancy of 26000 was used, which is an averaged molar absorbancy with a relatively narrow distribution of double conjugated dienic components. The molar absorbancy used for component U4 was assumed to be comparable to the molar absorbancy of the identified oxooctadecadienoic acids, because component U4 probably is an other unidentified isomer and the value of 21000 is again an reliable average value.

5.7.1 Composition of feed mixtures.

Based on the above considerations the composition of the feed mixture could be determined. The PV of batch II was 2775 mol m\(^{-3}\). Since 100% purity would require a PV of 3205 mol m\(^{-3}\), the feed mixture consists for 86.7% of the four hydroperoxides. 13-c,t-HPOD attributes for 80.6% to this percentage, while the other 6.1% comes from the other isomers. Furthermore 1.6% of 13-c,t-HOD and 1.3% of 13-c,t-OOD is present in the feed mixture derived from batch II. 10.4% of the feed mixture is unaccounted for and may consist of some dimers, unoxidised linoleic acid and components, insensitive to UV-detection, formed during production, isolation or storage of the material.

The composition of batch I is much more complex, as was already indicated by the GPC results described in paragraph 5.6.4. It consists for 48.5% of HPOD isomers, 11.7% not being the isomer expected form the enzymatic oxidation. The PV of batch

<table>
<thead>
<tr>
<th>Component</th>
<th>Batch I</th>
<th>Batch II</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-c,t-HPOD</td>
<td>36.8</td>
<td>80.6</td>
</tr>
<tr>
<td>13-t,t-HPOD</td>
<td>4.0</td>
<td>1.9</td>
</tr>
<tr>
<td>9-c,t-HPOD</td>
<td>2.9</td>
<td>2.4</td>
</tr>
<tr>
<td>9-t,t-HPOD</td>
<td>4.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Total HPOD</td>
<td>48.5</td>
<td>86.7</td>
</tr>
<tr>
<td>13-c,t-HOD</td>
<td>12.6</td>
<td>1.6</td>
</tr>
<tr>
<td>13-c,t-OOD</td>
<td>4.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Unknown</td>
<td>34.2</td>
<td>10.4</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>PV [mol m(^{-3})]</td>
<td>2075</td>
<td>2775</td>
</tr>
</tbody>
</table>

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I is 2075 mol m$^{-3}$, of which 1555 mol m$^{-3}$ can be attributed to the HPOD isomers. These data indicate that 520 mol m$^{-3}$ of hydroperoxide are present in other forms than the four HPOD isomers. This can be explained by the presence of dihydroperoxides or dimers containing hydroperoxide groups, of which examples are depicted in Figure 5.10.

5.7.2 Analysis procedure applied for routine quantification of reaction mixtures.

For the quantification of the reaction mixtures resulting from treated hydroperoxide samples four methods were applied on a routine basis, HPLC-UV with quantification of the components listed in Figure 5.8 with the procedure described earlier in this paragraph, the purge-and-trap analysis to determine the hexanal concentration, the Karl-Fischer method to determine the water concentration and the PV determination. Incidentally more volatiles were quantified by the procedure described in par 5.4.

5.8 Definitions

The conversion of linoleic acid hydroperoxide is for practical purposes related to the total concentration of the 4 HPOD isomers. A batch reactor was used, leading to the following equation describing the conversion:

$$X = \frac{n_{\text{HP}0D,0} - n_{\text{HP}0D,1}}{n_{\text{HP}0D,0}} = \frac{C_{\text{HP}0D,0} - C_{\text{HP}0D,1}}{C_{\text{HP}0D,0}}$$

(5.3)

The term on the right of this equation is used, since during reactions samples are taken, which affect the amount of the components present, but not their concentrations. Since a proportional amount of catalyst is taken as well by sampling the catalyst concentration also remains constant. The selectivity of a product is defined by:

$$S = \frac{n_{i,t} - n_{i,0}}{n_{\text{HP}0D,0} - n_{\text{HP}0D,1}} = \frac{C_{i,t} - C_{i,0}}{C_{\text{HP}0D,0} - C_{\text{HP}0D,1}}$$

(5.4)

Although most products are absent in the feed mixture, i.e. $C_{i,0} = 0$, this is not the case for the hydroxy- and oxooctadecadienoic acids, which are present as impurities in little or larger amounts in the different batches used as feed mixture for the experiments. The initial selectivity, $S_{i,0}$, is the selectivity at 0% conversion and is determined by extrapolation of the selectivity vs. conversion graphs to 0% conversion. The selectivity at 100% conversion, $S_{i,100}$, is also used as parameter and is obtained by extrapolation of the selectivity vs. conversion graphs towards 100% conversion. The final selectivity refers to the selectivity at the end of the experiment when generally all reactions have come to a complete stop.
The yield of a component is determined by the selectivity times the conversion:

\[ Y_i = S_i \times X \]  
(5.5)

The carbon balance of the reaction mixtures is determined by summation of the concentrations of the quantified components times the number of carbon atoms per molecule, assuming inertness of the MCT-oil:

\[ M = \sum_i C_{i1} m_i \times \sum_i C_{i0} m_i \times 100\% \]  
(5.6)

Carbon balances instead of mass balances are used since smaller molecules without carbon, like oxygen, hydrogen peroxide and water, are generally not measured.

Since the reaction rate equation is not known for most reactions, disappearance and production rates are used instead of reaction rates and are expressed either volumetrically or specifically. The relation between the volumetric and the specific production rate of component i is:

\[ R_{v_i} = \frac{dC_i}{dt} = R_{w_i} \times C_{\text{cat}} \]  
(5.7)

The production and disappearance rates are determined by the tangents of the concentration vs. time curves. In some cases the disappearance rate could globally be described as a first order reaction:

\[ R_{v_{\text{HPOD}}} = r_v = k_v \times C_{\text{HPOD}} = k_w \times C_{\text{HPOD}} \times C_{\text{cat}} \]  
(5.8)

This allowed to calculate the global apparent activation energy via the Arrhenius equation:

\[ k = A \exp \left( \frac{-E_{\text{act}}}{RT} \right) \]  
(5.9)

References

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- Denney D.B., Goodyear W.F. and Goldstein B., "Concerning the mechanism of the reduction of hydroperoxides by trisubstituted phosphines and trisubstituted phosphites". JACS 82 (1959), 1393-1395.
6

THERMAL CONVERSION OF 13-HYDROPEROXY-9-CIS,11-TRANS-OCTADECADIENOIC ACID

6.1 Introduction

As a consequence of the processing, transport and storage of raw edible oils under aerobic conditions, oxidised fatty acids are present in the oils in the form of hydroperoxides. During refining, these hydroperoxides are predominantly removed in the bleaching step, which is carried out at moderate temperatures of 343 - 383 K. The hydroperoxides left after bleaching will be removed during the deodorisation step in which temperatures higher than 473 K are employed. The kinetics and the mechanisms of the thermal reactions that the hydroperoxides are subject to under the former temperatures have been studied and the results are reported in this chapter. The methods described in chapter 5 were used in order to obtain these results, and will be related to similar studies summarised in chapter 2. All experiments were carried out under nitrogen atmosphere to exclude new oxidation reactions and to resemble refining conditions as much as possible. As mentioned before, 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid (13-c,t-HPOD) was used as model hydroperoxide in MCT-oil as solvent.

6.2 Construction of the reaction network

In paragraph 5.6 the identification of the non-volatile reaction products of 13-c,t-HPOD has been described. The components that were formed thermally at 393 K
and that have been identified completely are depicted in Figure 6.1. Most of these components were found in earlier studies, see e.g. Gardner (1987), although the exact isomeric structure often was not elucidated. By analysis of the evolution of these main reaction products vs. batch time, their selectivities vs. the conversion and the formation of volatile products, the reaction network has been constructed.

\[
\begin{align*}
13\text{-hydroxy-9-cis,11-trans-octadecadienoic acid} & \quad (13\text{-c,t-HOD}) \\
13\text{-hydroxy-9-trans,11-trans-octadecadienoic acid} & \quad (13\text{-t,t-HOD}) \\
9\text{-hydroxy-10-trans,12-cis-octadecadienoic acid} & \quad (9\text{-c,t-HOD}) \\
9\text{-hydroxy-10-trans,12-trans-octadecadienoic acid} & \quad (9\text{-t,t-HOD}) \\
13\text{-oxo-9-cis,11-trans-octadecadienoic acid} & \quad (13\text{-c,t-0OD}) \\
13\text{-oxo-9-trans,11-trans-octadecadienoic acid} & \quad (13\text{-t,t-0OD}) \\
9\text{-oxo-10-trans,12-cis-octadecadienoic acid} & \quad (9\text{-c,t-0OD}) \\
9\text{-oxo-10-trans,12-trans-octadecadienoic acid} & \quad (9\text{-t,t-0OD}) \\
9\text{-trans,11-trans,13-trans-octadecadienoic acid} & \quad (13\text{-c,t-000}) \\
13\text{-oxo-9-cis,11-trans-tridecadienoic acid} & \quad (13\text{-c,t-OTD}) \\
13\text{-oxo-9-trans,11-trans-tridecadienoic acid} & \quad (13\text{-t,t-OTD}) \\
2\text{-trans,4-trans-decadienal} & \quad (DD)
\end{align*}
\]

\[
R_1 = \text{CH}_3(\text{CH}_2)_3; \quad R_2 = (\text{CH}_2)_6\text{C(O)OH}
\]

**Figure 6.1** List of identified non-volatile thermal reaction products of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid.

Based on the information obtained and outlined in the following, the network for the thermal conversion of 13-c,t-HPOD, so far elucidated, is constructed. This network is shown in Figure 6.2. Primary products range from smaller cleaved molecules, such as hexanal and OTD, via the C\(_{18}\)-products, HOD and OOD, to oligomeric products. It was furthermore observed that the polyunsaturated products are subject to further reactions, such as polymerisations. For 9-HPOD, which is for ±4.3% present in the feed mixture, the corresponding network is observed. The global kinetics of the network will be discussed and mechanisms will be proposed for the formation of the observed products.
Chapter 6
Thermal conversion of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid

Figure 6.2 Proposed reaction network for conversion of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid (13-c,t-HPOD).

Hydroperoxyoctadecadienoic acids (HPOD)
In Figure 6.4 a typical result is shown of a batch experiment in which 13-c,t-HPOD is thermally converted. In this graph the total concentration of the different isomers of the main products is depicted for the conversion at 393 K in MCT-oil. The disappearance of the hydroperoxide isomers globally follows a first order reaction, indicated by the good fit of the exponential curve through the experimental data points. This first order reaction is described by the equation:

$$\frac{dC_{\text{HPOD}}}{dt} = -k_1 \cdot C_{\text{HPOD}} \quad (6.1)$$

in which $k_1$ is the global first order reaction rate coefficient, which amounts to $5.2 \times 10^{-5}$ s$^{-1}$. This means that at a temperature of 393 K the hydroperoxide is converted on a time scale of several hours to a day. From Figure 6.3 it is concluded that during the conversion no other hydroperoxides are formed, since the total hydroperoxide concentration equals within experimental error the concentration of the four HPOD isomers.
The montmorillonite catalysed conversion of hydroperoxides

Figure 6.4 Concentration vs. batch time for main reaction components during thermal conversion of 13-cis-HPOD at 393 K in MCT-oil. Abbreviations see Figure 6.1.

Figure 6.5.a-d shows the evolution of the individual isomers during thermal conversion. From regression of the disappearance curves of the hydroperoxide isomers, shown in Figure 6.5.a, by a global first order equation, see equation 4.1, it was concluded that the rate coefficients are a little higher for the cis,trans than for the trans,trans isomers, 5.2 resp. 4.8 $10^{-5}$ s$^{-1}$. This indicates little but otherwise negligible isomerisation of the cis,trans-towards the trans,trans-isomers or that the trans,trans-isomers are a little more stable towards thermal conversion. Figure 6.5 furthermore leads to the conclusion that no isomerisation between the positional hydroperoxy-isomers occurs. This result is in contrast to the studies of Chan et al. (1979), in which significant isomerisation was found, although lower temperatures were employed. In the presented results, the conversion may have become more important than the isomerisation as a consequence of a higher activation energy.

Figure 6.3 Concentration of total and linoleic acid hydroperoxides vs. batch time for the thermal conversion at 393 K in MCT.
Cleavage products: oxotridecadienoic acids (OTD), hexanal and decadienal (DD)

It appeared that cleavage of the hydroperoxide was the main mechanism, leading to the products OTD and hexanal with initial selectivities of 17.0 and 14.2 mol %, see Figure 6.4, Figure 6.5, Figure 6.6 and Table 6.1. This cleavage most probably proceeds by the \( \beta \)-elimination mechanism of the 13-alkoxy radical described in paragraph 2.4.2, see Frankel (1984). Since hexanal and OTD are formed in comparable amounts, the \( \beta \)-elimination as shown in Figure 2.4 apparently occurs to the same degree by type a and type b. Simultaneously with OTD a C\(_5\)-product, most probably pentane, is formed, but this component could not be detected due to reasons outlined below. Together with hexanal a C\(_{12}\)-product has to be formed, most probably 12-oxo-9-cis-dodecenoic acid. This component could however not be detected, either because of its lack of conjugation or volatility. The conditions employed apparently did not allow isomerisation of this isomer to the 12-oxo-10-trans-dodecenoic acid isomer, which would be detected due to its conjugation and which has been found as thermal reaction product under more severe conditions (Frankel, 1980).
Decadienal is formed by the β-elimination mechanism similar to the oxotridecadienoic acids, in this case from the 9-alkoxy radical. The fact that the ratio of the 13- to 9-HPOD isomers in the feed mixture is almost equal to the ratio of OTD to DD being formed, confirms the previous conclusion that isomerisation between the hydroperoxy isomers is not important under the conditions employed. The ratio would have been lower if this was the case.

Figure 6.5.d displays the course of the individual OTD isomers. It is clear that the trans,trans-isomer is formed in larger amounts than the cis,trans-isomer. The ratio of the initial selectivities towards the cis,trans and trans,trans isomers is 0.56, which is much higher than the original 13-c,t-HPOD to 13-c,t-HPOD ratio of 0.05. This indicates that the β-elimination mechanism by which these components are formed, does not retain the original stereochemical configuration. While the concentration of 13-c,t-OTD appears to become constant, the concentration of 13-t,t-OTD keeps increasing. From this observation the occurrence of isomerisation between the kinetically favoured cis,trans-isomer to the thermodynamically more stable trans,trans-isomer is concluded.

<table>
<thead>
<tr>
<th>Component</th>
<th>Initial selectivity [mol %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-c,t-HOD</td>
<td>6.3</td>
</tr>
<tr>
<td>13-t,t-HOD</td>
<td>&lt; 0.3</td>
</tr>
<tr>
<td>9-c,t-HOD</td>
<td>0.9</td>
</tr>
<tr>
<td>9-t,t-HOD</td>
<td>0.8</td>
</tr>
<tr>
<td>13-c,t-OOD</td>
<td>10.1</td>
</tr>
<tr>
<td>13-t,t-OOD</td>
<td>0.8</td>
</tr>
<tr>
<td>9-t,t-OOD</td>
<td>0.3</td>
</tr>
<tr>
<td>13-c,t-OTD</td>
<td>6.2</td>
</tr>
<tr>
<td>13-t,t-OTD</td>
<td>11.0</td>
</tr>
<tr>
<td>2,4-Decadienal</td>
<td>0.8</td>
</tr>
<tr>
<td>Hexanal</td>
<td>14.2</td>
</tr>
</tbody>
</table>
Hydroxy- (HOD) and oxooctadecadienoic acids (OOD)
The other main products are the hydroxy- (HOD) and oxooctadecadienoic acids (OOD). These components are formed in comparable amounts, especially in the early stages of the reaction, with the concentrations of OOD always being a little higher. These observations are in good agreement with earlier studies, see Gardner et al. (1974) and Hamberg et al. (1975). The explanation for the comparable amounts is that these products are formed together via the disproportionation reaction or the Russell mechanism described in paragraph 2.4.3, see Russell (1957) and Schieberle et al. (1981).

The 13-\textit{c},t-HOD is the most dominant of the HOD isomers formed, see Figure 6.5.b. This component has the same stereo configuration as the original hydroperoxide. Therefore a potential mechanism for the formation of this component is disproportionation, see paragraph 2.4.3, in which the stereo configuration also is retained (Dever and Calvert, 1962; Gardner and Crawford, 1981). From Figure 6.5.b it can also be concluded that no isomerisation between the HOD isomers occurs, since no increase in any of the other isomers is observed.

The behaviour of the OOD isomers is different, see Figure 6.5.c, although the 13-\textit{c},t-OOD isomer is the main isomer being formed. Retention of the isomeric configuration may again be explained by the disproportionation. In this case however isomerisation between the \textit{cis},\textit{trans} and \textit{trans},\textit{trans} isomers appeared to occur. This was concluded from the simultaneous decrease of 13-\textit{c},t-OOD and increase of 13-\textit{t},\textit{t}-OOD in the final stages of the reaction. This again suggests that the formation of the \textit{cis},\textit{trans}-isomers is kinetically controlled, while the \textit{trans},\textit{trans}-isomers are thermodynamically more stable.

Other volatile reaction products
After 100% conversion the volatile components were identified and quantified, resulting in the data shown in Table 6.11. The main fraction consists of (unsaturated) aldehydes and fatty acids. This list is in good agreement with results obtained in earlier studies, see Frankel et al. (1981) and Grosch (1987). The decadienal concentration determined by this method is equal to the concentration resulting from HPLC-UV (0.15 mol m$^{-3}$). Hexanal and decadienal are with 2-trans-octenal the main aldehydes. 2-trans-octenal may be formed from degradation of decadienal, see Grosch (1981). The formation of the other aldehydes is more difficult to explain.

The main fatty acids are hexanoic and octanoic acid. The formation of octanoic acid may be explained by some hydrolysis of the MCT-oil and by $\beta$-elimination of the 9-hydroperoxy isomer. The origin of hexanoic acid is more complex, but the oxidation of hexanal by the hydroperoxide is a possible explanation. Other identified volatiles are ethylbenzene, pentyl furane, methyl octanoate and 2,3-octadione.
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Table 6.11 Concentration of volatile products in mmol m\(^{-3}\) after thermal conversion of 28 mol m\(^{-3}\) 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid at 393 K in MCT-oil with a reaction time of 80 ks.

<table>
<thead>
<tr>
<th>Product</th>
<th>Concentration (mmol m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentanal</td>
<td>17.6</td>
</tr>
<tr>
<td>Hexanal</td>
<td>917.1</td>
</tr>
<tr>
<td>Heptanal</td>
<td>17.0</td>
</tr>
<tr>
<td>Octanal</td>
<td>7.1</td>
</tr>
<tr>
<td>Nonanal</td>
<td>6.8</td>
</tr>
<tr>
<td>t2-Heptenal</td>
<td>19.7</td>
</tr>
<tr>
<td>t2-Octenal</td>
<td>54.5</td>
</tr>
<tr>
<td>t2-Nonenal</td>
<td>6.5</td>
</tr>
<tr>
<td>t2-Decenal</td>
<td>16.8</td>
</tr>
<tr>
<td>t2,c4-Decadienal</td>
<td>17.0</td>
</tr>
<tr>
<td>t2,t4-Decadienal</td>
<td>143.4</td>
</tr>
<tr>
<td>2-Heptanone</td>
<td>12.5</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>11.3</td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>3.6</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>7.6</td>
</tr>
<tr>
<td>Butanoic acid</td>
<td>3.9</td>
</tr>
<tr>
<td>Pentanoic acid</td>
<td>28.8</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>1378.4</td>
</tr>
<tr>
<td>Heptanoic acid</td>
<td>33.4</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>566.4</td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>22.4</td>
</tr>
<tr>
<td>Total</td>
<td>3293.5</td>
</tr>
</tbody>
</table>

The total selectivity to volatile products related to the number of carbon atoms present in the volatiles is \(\pm 4\%\), which is in good agreement with results of Frankel et al. (1960). This selectivity may be higher if the formation of pentane is taken into account. Pentane is expected to be formed simultaneously with OTD, see 2.4.2, which has been shown to be a major product, see Figure 6.4. The analysis method however was not able to analyse highly volatile components such as pentane.

Consecutive reactions
A remarkable phenomenon is the decrease in the polyunsaturated products, such as HOD and OOD, OT, OTD and DD after longer reaction times. Figure 6.6 furthermore clearly indicates a strong decrease of the selectivity towards these products vs. the conversion. Therefore, it can be concluded that these products undergo consecutive reactions for which polymerisation reactions are the most probable due to the unsaturations of these components.

More striking is the fact that the decrease in the selectivity vs. the conversion is linear and occurs parallel for the main products: HOD, OOD and OTD. These observations are difficult to explain since, if these products are subject to subsequent reactions, for any reaction order a more than linear decrease in the selectivity vs. the conversion is expected.

Conclusions
The total initial selectivity towards the products tabulated in Table 6.1, corrected for the number of carbon atoms present in the molecule, amounts to 37.1%, indicating that 62.9% was not identified. Thereof 14.9% can be attributed to the non-detected parts of the cleavage reactions to OTD and hexanal, as discussed in the previous paragraph. A few percent of the deficiency can furthermore be ascribed to the other volatile products, for which no initial selectivities could be determined. The remaining gap can be explained by the formation of non-UV sensitive products such as epoxyhydroxyoctadecenoic acids, according to the mechanisms described in
paragraph 2.4.3, and the formation of oligomers, which presence was shown by GPC-MS, see paragraph 5.6.4. Because the main identified products undergo consecutive reactions towards components that were not identified, the carbon balance decreases during conversion. At 100% conversion the carbon balance amounts to only 12.5%.

6.3 The effect of the process conditions

Several process conditions have been varied to study their effect on the thermal conversion. By changing the temperature the apparent activation energy could be determined. The water concentration and the solvent were varied to determine the effect of the medium.

6.3.1 Temperature

Thermal conversions were carried out in the temperature range of 333 - 413 K. Global first order rate coefficients were determined in the same way as described for the conversion at 393 K in paragraph 6.2. In Figure 6.7 these results are plotted as an Arrhenius plot, see also Equation 5.10. Both feed mixtures from batch I and II were used for studying the effect of the temperature. From Figure 6.7 it can be concluded that although the composition of these mixtures is different, the hydroperoxide present is converted at the same rate for both batches. From the slope of the linear relationship between the ln(k1) and the reciprocal temperature, the apparent activation energy was calculated, and amounted to 90.7 kJ mol⁻¹. Due to lack of comparable studies this number cannot be related to previous results.

In the range of temperatures applied the same products were always found, although their ratio varied. In all cases the selectivity decreased with the conversion, although this was not always linear, as was the case in the example shown in Figure

![Figure 6.7](image-url)  
Figure 6.7 Arrhenius plot of global first order reaction rate for thermal conversion of 13-c1-HPOD. Markers: experimental points from ■: batch I and ●: batch II; line: linear regression result.
6.6. More often this decrease was more pronounced in the early stages of the conversion. Due to the fact that this relationship was not linear, the initial selectivities were determined with relatively large errors. The initial selectivities for the main products are shown as a function of the temperature in Figure 6.8.

The initial selectivity towards OTD and DD increases with temperature. This is in agreement with the results of Kimoto and Gaddis (1974) and Henderson et al. (1980). It furthermore indicates that the activation energy for the formation of these products is higher than the average activation energy. Remarkable is that the initial selectivity towards these cleavage products is lower for batch II. This can be explained by formation of these products from other components present in the feed mixture of batch I.

The initial selectivity towards OOD decreases with temperature, while the initial selectivity to HOD displayed a more complex relationship with temperature. The latter component did not form at 333 K and after going through a maximum of ±12% the initial selectivity decreases at higher temperatures. This phenomenon indicates a change in the rate determining step for the hydroxy component. The decrease in the selectivity for HOD at higher temperatures and OOD suggests a lower than average activation energy for their formation.

6.3.2 Solvent and water concentration

In Figure 6.9 the HPOD concentration is plotted against batch time for the thermal conversion in different solvents. It appeared that the conversion was faster in decane and cumene than in MCT-oil, while the conversion was equally fast in cumene and decane. This observation may be related to the polarity of the solvents used, for MCT-oil is more polar than the other solvents. The slower conversion in
more polar solvents may be explained by stabilisation of the hydroperoxide by the polar groups in the solvents. It is furthermore interesting that the conversion in decane and cumene were equally fast. Cumene is a very good hydrogen donor, but this property apparently does not affect the conversion rate, i.e. in the rate determining steps no hydrogen donation takes place.

A higher water concentration of 120 mol m$^{-3}$, which approaches the maximum solubility, led to a small decrease in the conversion rate of the hydroperoxides compared to a water concentration of 15 mol m$^{-3}$, which is the concentration in the commercially obtained MCT-oil. This result corresponds to the effect of the solvent, in which a more polar solvent inhibited the thermal conversion of HPOD, for a higher water concentration can be considered as a more polar solvent medium.

The initial selectivity is also affected by the solvent, see Figure 6.10. This is most dramatic for the $\beta$-elimination towards OTD and DD. In cumene the initial selectivity towards OTD is 19%, followed by 15% in MCT and a low selectivity of 5% in decane. The selectivity towards DD follows the same trend. No plausible explanation for this observation can be advanced. It was furthermore remarkable that in decane the selectivity towards these cleavage products increased with the conversion in contrast to all other conditions in which the reverse was observed, as described in paragraph 6.2. This indicates that an intermediate is involved via which these products can be formed.

The selectivity towards HOD is not significantly different for the different solvents, which is remarkable in view of the strong hydrogen donating ability of cumene and the potential mechanism described in paragraph 2.4.3, which is based on hydrogen donation. As was concluded at that time, this mechanism is of little importance in
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Figure 6.10 Initial selectivities for main products during thermal conversion of HPOD in different solvents.

realistic systems. The reaction towards OOD is mostly favoured in decane, with no significant difference between its selectivity in MCT-oil and cumene.

6.4 Conclusions

Thermal conversion of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid leads to a complex mixture of reaction products, involving oligomers, products in which the C₁₈-chain is maintained but in which the functionality has changed, and cleaved products. The reaction network is for a large part elucidated by detailed analysis of the kinetic experiments. Cleavage according the β-elimination mechanism is the main reaction. The higher unsaturated products are subject to polymerisation reactions. No isomerisation between hydroperoxide isomers occurs, but oxodienic products are subject to cis-trans isomerisation.

The activation energy for thermal conversion is 90.7 kJ mol⁻¹. The temperature furthermore affects the selectivity. More cleavage products, tridecadienoic acids and decadienal, and less oxooctadecadienoic acids are formed at higher temperatures. More polar solvents inhibit the conversion to some degree. The selectivity towards cleavage products decreases in the following order: cumene > MCT-oil > decane. Other selectivities are less affected by the solvent type.

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DEACTIVATION OF MONTMORILLONITES DURING THE CONVERSION OF HYDROPEROXYOCTADECADIENOIC ACID

7.1 Introduction

It is often observed that solid acid catalysts deactivate during reaction (Froment and Bischoff, 1990). During deactivation of solid acid catalysts, commonly, polyaromatic components with low H/C-ratios are formed on the catalyst surface, which are irreversibly adsorbed, thereby poisoning the catalyst. Therefore deactivation is often referred to as "coking". The deactivation may occur on a time scale varying from seconds to months. Regeneration is often required to enable economic profitable processes. Because zeolites are relatively easy to regenerate they have overtaken clay minerals as catalysts for most cracking purposes in mineral oil refineries, in which regeneration is essential. Due to the layered structure of clay minerals, which are kept at a distance from each other by solvent molecules such as water, the structure collapses if this water is removed by for example high temperatures causing the catalyst to lose its activity. For many other applications such as in the field of the fine chemistry clay minerals have gained interest however. Their mesoporous structure has advantages over the microporosity of zeolites especially when larger molecules are involved, while the acid strength is comparable (Tanabe, 1970). New developments have led to the pillared clay minerals in which the mesoporous structure is retained by the introduction of pillars. By varying the pillars the properties of the catalysts can easily be adjusted (Schoonheydt, 1991).
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For edible oil refining purposes always clay minerals have been used. Due to the irreversible adsorption of certain oil constituents, especially coloured components such as chlorophyll and carotene, the montmorillonite loses its activity, which cannot be regenerated. In this chapter it will be shown that the reactions that occur during the conversion of hydroperoxides in the bleaching step of the refining process also contribute to the deactivation of the montmorillonite. Paragraph 7.3 shows the large effect of this phenomenon on the reaction rate, whereas in paragraph 7.4 the relation between the physical properties of the catalyst and its activity is determined. The differences in the degree of the deactivation of the different montmorillonites used are discussed in paragraph 7.5. The effect of the process conditions will shortly be described in paragraph 7.6 and a simple model which can describe the deactivation will be presented in paragraph 7.7. The experimental and analytical procedures and the catalyst characterisations used in this chapter were performed according to the procedures discussed in chapter 5.

7.2 Deactivation phenomena

Two main mechanisms of deactivation by coking can be discerned. Parallel deactivation occurs when the reactant or other components preceding the rate determining step are responsible for the coke formation. A process is called consecutive or series deactivation if the products give rise to coke formation. The deposition of coke may deactivate the catalyst by site coverage or pore blockage and may furthermore be complicated by the occurrence of diffusional limitations. These aspects and their influence on the kinetics of the process has been extensively studied, see for example Froment and Bischoff (1990).

An obvious way of expressing the deactivation by coke formation in the absence of diffusional limitations is by the ratio of the chemical reaction rates $r/r_0$, represented by $\Phi$, the deactivation function:

$$\Phi = \frac{\text{reaction rate with present catalyst}}{\text{reaction rate with fresh catalyst}} = \frac{r}{r_0} \quad (7.1)$$

This relation is valid if the reactant concentrations are kept constant, as is the case in continuous reactors. Since in this thesis batch reactions have been carried out, the reaction rate has to be corrected for the decrease in the reactant, i.e. the hydroperoxide concentration. This practically means that $\Phi$ was determined by dividing the apparent first order reaction rate coefficient $k$ at a given time by the apparent first order reaction rate coefficient of the fresh catalyst, $k_0$. The apparent first order reaction rate coefficients were determined by dividing the tangent of the HPOD vs. batch time curves by the HPOD concentration at that time. $\Phi$ is represented in this chapter as a percentage of the rate with the fresh catalyst.
The coking reaction itself may also be subject to deactivation, generally expressed as:

\[ \Phi_c = \frac{\text{coking rate with present catalyst}}{\text{coking rate with fresh catalyst}} = \frac{r_c}{r_{c,0}} \]  

(7.2)

The two relations 7.1 and 7.2 involve four characteristics of a reaction subject to deactivation. Whereas \( r \) represents the rate of the main reaction, \( \Phi \) is a measure for the deactivation of the main reaction. \( r_c \) is the coking rate, the deactivation of which is represented by \( \Phi_c \). Although a general approach has been developed by the group of Froment to relate these observations to the characteristic features of the reactions and of the catalyst (Froment and Bischoff, 1990), often more empirical relations are introduced for \( \Phi \). In the most simple approach \( \Phi \) is expressed as a function of reaction time \( \Phi = f(t) \), while in a more direct approach in which the carbon content of the catalyst has been monitored, \( \Phi \) may be expressed as a function of the carbon content: \( \Phi = f(C_c) \). The following forms, proposed by Froment and Bischoff (1962) are examples of relations which are often used:

\[ \Phi = \exp(-\alpha C_c) \]

\[ \Phi = \frac{1}{1 + \alpha C_c} \]

In this chapter the phenomena described in this paragraph will be elucidated for the deactivation of montmorillonites during the conversion of hydroperoxyoctadecadienoic acid (HPOD).

### 7.3 Deactivation

The first indications for the occurrence of deactivation of the montmorillonite during the conversion of HPOD were the browning of the catalyst during reaction, which is a typical observation, and the fact that the disappearance curve of HPOD could not be described by a simple rate equation. Confirmation was obtained by the results shown in Figure 7.1, in which after certain reaction times new HPOD was added to the reactor. It is easily seen that the second portion of HPOD is converted much slower than the first by the same portion of catalyst.

In order to evaluate whether the reaction products present in the reaction mixture were responsible for the slower conversion of the second portion, for example by competitive adsorption, conversions were carried out in fresh and used MCT-oil, containing reaction products of a previous conversion, and with fresh Supreme FF and Supreme FF once used for a previous conversion. After this conversion the
Figure 7.1 HPOD concentration vs. batch time during Supreme FF (5 kg m⁻³) catalysed conversion at 363 K in MCT-oil. At a batch time of 3 ks new HPOD was added to the reactor. Markers: experimental data points, curves: calculated by Equations 7.7 - 7.11 and with the parameters reported in Table 7.VII.

catalyst was filtered off, thoroughly washed with large amounts of hexane (Riedel-de Haen, p.a.) and dried at 363 K under air for 30 min prior to renewed use.

From Figure 7.2 it can be concluded that the slower conversion of the second portion of HPOD is not caused by the presence of reaction products at the start of the conversion, i.e. factors such as competitive adsorption are not important. The conversions of HPOD with fresh catalyst proceed equally fast with or without the presence of reaction products. This fact also leads to the suggestion that the

Figure 7.2 HPOD concentration vs. batch time during the Supreme FF (5 kg m⁻³) catalysed conversion at 363 K in fresh MCT-oil and used MCT-oil containing products from a previous reaction and with fresh catalyst or used catalyst from a previous reaction. Markers: experimental data points, curves: calculated by Equations 7.7 - 7.11 and with the parameters reported in Table 7.VII.
reaction products present in the solvent matrix are not involved in the reactions causing the deactivation, otherwise the deactivation would have been more important for the conversion in the presence of those reaction products, i.e. in the used MCT-oil.

7.4 Relation between the activity and the physical properties of the catalyst during deactivation

To obtain more insight in the process of the deactivation, the properties of the Supreme FF catalyst were studied as a function of the batch time, see Figure 7.3. During reaction relatively large samples were taken, from which the catalyst was filtered off. Subsequently the catalyst was washed with hexane and dried for 30 min prior to the analyses. To determine the properties of the catalyst at a batch time of \( t = 0 \) s, Supreme FF was suspended in MCT-oil without HPOD at 363 K and subsequently subjected to the procedure described above. It appeared that by suspending the catalyst in MCT-oil, material corresponding to 6.1% (w/w) carbon is irreversibly deposited on the catalyst surface, thereby diminishing the BET surface area \( (A_{\text{BET}}) \) from 320 to 205 \( \text{m}^2 \text{g}^{-1} \) and the pore volume \( (V_{\text{pore}}) \) from 0.489 to 0.290 \( \text{cm}^3 \text{g}^{-1} \). Possible explanations for this deposition are filling of the smaller pores, from which the triglycerides are hardly desorbed, or irreversible adsorption of traces of polar components, such as mono- and diglycerides on the catalyst surface.

From Figure 7.3 it is clear that in the first 500 s the BET surface area and the pore volume dramatically decrease and the carbon content \( (C_c) \) dramatically increases. From the original BET surface area of 205 \( \text{m}^2 \text{g}^{-1} \) only 30 \( \text{m}^2 \text{g}^{-1} \) remains, while the...
pore volume decreases from 290 to 70 cm$^3$ g$^{-1}$. This decrease is caused by deposition of material causing 11% (w/w) carbon on the catalyst. This amount corresponds to ± 8% of the original HPOD present in the reactor. From the decrease of the BET surface area and the pore volume it is concluded that due to this deposition pores are filled or that the entrances of the pores are blocked.

In Figure 7.3 also the deactivation function $\Phi$ is plotted vs. batch time. The value for $\Phi$ is determined according to the procedure described in paragraph 7.2. The curve of $\Phi$ vs. batch time shows a dramatic decrease of $\Phi$. The curve corresponds furthermore very well with the BET surface area vs. batch time curve, suggesting a direct relationship between $\Phi$ and the BET surface area. When $\Phi$ is depicted vs. the BET surface area with all data obtained for the Supreme FF catalysed conversions in MCT-oil at 363 K, the graph shown in Figure 7.4.a is obtained. These results show that during deactivation, above a BET surface area of 30 m$^2$ g$^{-1}$, a linear relationship exists between the deactivation function $\Phi$ and the BET surface area. Below this value the BET surface area and $\Phi$ are determined with relative large errors.

![Figure 7.4](image)

*Figure 7.4* Deactivation function $\Phi$ vs. a BET surface area, b Carbon content and c Pore Volume of deactivated Supreme FF during the conversion of HPOD at 363 K in MCT-oil. d Relation between the physical properties.
Furthermore the external BET surface area remains taken into account since by physisorption no distinction can be made between a clean surface and a surface on which material has been deposited. The linear relation between the BET surface area and $\Phi$ is given by:

$$\Phi = -15.5 + 0.565 \, A_{\text{BET}}$$

No linear relationship was found for $\Phi$ vs. the pore volume or the carbon content, see Figure 7.4.b and Figure 7.4.c. $\Phi$ appeared to depend more strongly on the pore volume at larger pore volumes than at lower pore volumes. For the carbon content the reverse was observed.

The varying degrees of deactivation were obtained by variation of reaction time, catalyst concentration and initial HPOD concentration. It appeared that when the initial concentration of HPOD was higher or when the catalyst concentration ($C_{\text{cat}}$) was lower the degree of deactivation increased, see Figure 7.5 for the effect of the catalyst concentration. Although from this Figure it is not that evident that the degree of deactivation is much more pronounced at lower catalyst concentrations, the catalyst properties as shown in Table 7.1 clearly indicate this trend. Since it furthermore appeared that the HPOD concentration affected the deactivation function, it could be concluded that HPOD or other components preceding the rate determining step of the conversion are involved in the reactions causing the deactivation. This indicates that the deactivation is caused by what is called parallel deactivation (Froment and Bischoff, 1990).

![Figure 7.5 Effect of Supreme FF concentration on the conversion of HPOD at 363 K in MCT-oil. Markers: experimental data points, curves: calculated by Equations 7.7 - 7.11 and with the parameters reported in Table 7.VII.](image-url)
Table 7.1 Supreme FF properties after complete conversion HPOD ($C_0 = 32$ mol m$^{-3}$) from batch II at 363 K in MCT-oil, with varying catalyst concentration.

<table>
<thead>
<tr>
<th>$C_{\text{cat}}$ [mol m$^{-3}$]</th>
<th>Batch time [ks]</th>
<th>$C_C$ [w/w%]</th>
<th>$A_{\text{BET}}$ [m$^2$ g$^{-1}$]</th>
<th>$V_{\text{pore}}$ [cm$^3$ g$^{-1}$]</th>
<th>$d_{\text{pore}}$ [nm]</th>
<th>$\Phi$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>80</td>
<td>21.5</td>
<td>31.2</td>
<td>0.030</td>
<td>13.5</td>
<td>2.8</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>17.1</td>
<td>41.2</td>
<td>0.090</td>
<td>11.5</td>
<td>12.5</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>14.5</td>
<td>68.1</td>
<td>0.150</td>
<td>9.7</td>
<td>33.6</td>
</tr>
</tbody>
</table>

From Figure 7.3 it was already clear that by deactivation the BET surface area decreases. From Figure 7.6 in which the average pore diameter ($d_{\text{pore}}$) is shown vs. the BET surface area for Supreme FF, deactivated to different degrees, it is concluded that at lower values of the BET surface area, i.e. more pronounced deactivation, the average pore diameter increases. This indicates that during deactivation the smaller pores are filled or blocked before the larger ones. In combination with the observation that the deactivation function is linearly related to the BET surface area, it can be concluded that the catalytic active sites are homogeneously distributed over the pores of the catalyst particle, both with respect to the location as with respect to the acid strength.

![Figure 7.6 Average pore diameter vs. BET surface area of Supreme FF deactivated during the conversion of HPOD in MCT-oil.](image)

The nature of the deposited material has not been elucidated, but the H/C-ratio of this material, which is plotted vs. the carbon content in Figure 7.7, is rather high. This ratio is ±1.5, which is somewhat lower than the H/C-ratio of 1.78 of the original HPOD. This indicates that upon deactivation roughly 4 hydrogen atoms per molecule of hydroperoxide are lost due to dehydrogenation. The H/C-ratio furthermore appeared to be almost independent of the carbon content, i.e. independent of the degree of deactivation. This suggests that as the deactivation proceeds, hardly any further dehydrogenation of the deposited species takes place.
Deactivation of montmorillonites during conversion of hydroperoxyoctadecadienoic acid

7.5 The effect of the montmorillonite type

Several montmorillonite types have been applied for the conversion of HPOD. Their physical properties were determined to evaluate possible differences in the process of deactivation, which may have occurred for example due to differences in the acidity. The results of the catalyst characterisations are shown in Table 7.11. All catalysts appeared to lose part of their available surface area and pore volume by suspending in MCT-oil without reactant as was also the case for Supreme FF. This loss is independent of the suspension time and catalyst concentration. Therefore, the deactivation function of the catalysts suspended in MCT-oil without reactant was defined as being 100%.

During the conversion of HPOD all catalysts deactivated. The BET surface area decreased to a comparable degree for all catalysts, i.e. to 30 - 50% of the original value. The deactivation function after complete conversion of HPOD corresponded again very well with the BET surface area, except for ACC FF. For this catalyst a value for the deactivation function of 7.6% was found. This lower value can be explained by the slower conversion of HPOD leading to a higher time averaged concentration of the hydroperoxide. It was concluded in the previous paragraph that the deactivation occurs by parallel deactivation, which means that at higher average HPOD concentrations more deactivation may take place, under the condition that the deposition rate is less dependent on the acidity than the conversion. The fact that this is not observed for B-80 can be explained by its different structure with larger pores, which are less readily blocked or filled.
The montmorillonite catalysed conversion of hydroperoxides

Table 7.11 Properties of different catalysts used at a concentration of 10 kg m\(^{-3}\) after complete conversion of HPOD (C\(_0 = \pm 30\) mol m\(^{-3}\)) from batch II at 363 K in MCT-oil.

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Batch time [ks]</th>
<th>C(_C) [w/w%]</th>
<th>(A_{\text{BET}}) [m(^2)g(^{-1})]</th>
<th>(V_{\text{pore}}) [cm(^3)g(^{-1})]</th>
<th>(d_{\text{pore}}) [nm]</th>
<th>(\Phi) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supreme FF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fresh</td>
<td>0.1</td>
<td>321</td>
<td>0.461</td>
<td>6.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>suspended</td>
<td>6.3</td>
<td>206</td>
<td>0.291</td>
<td>6.3</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>used</td>
<td>25</td>
<td>14.5</td>
<td>68.1</td>
<td>0.150</td>
<td>9.7</td>
<td>33.6</td>
</tr>
<tr>
<td>XJ-9126</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fresh</td>
<td>0</td>
<td>314</td>
<td>0.444</td>
<td>6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>suspended</td>
<td>7.1</td>
<td>168</td>
<td>0.305</td>
<td>6.5</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>used</td>
<td>25</td>
<td>12.9</td>
<td>50.3</td>
<td>0.105</td>
<td>8.8</td>
<td>23.2</td>
</tr>
<tr>
<td>F-20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fresh</td>
<td>-</td>
<td>286</td>
<td>0.335</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>suspended</td>
<td>0</td>
<td>126</td>
<td>0.195</td>
<td>5.8</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>used</td>
<td>25</td>
<td>12.7</td>
<td>43.1</td>
<td>0.089</td>
<td>8.1</td>
<td>25.1</td>
</tr>
<tr>
<td>ACC FF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fresh</td>
<td>-</td>
<td>190</td>
<td>0.277</td>
<td>6.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>suspended</td>
<td>0</td>
<td>90.0</td>
<td>0.168</td>
<td>6.6</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>used</td>
<td>85</td>
<td>11.7</td>
<td>38.1</td>
<td>0.097</td>
<td>11.9</td>
<td>7.6</td>
</tr>
<tr>
<td>B-80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fresh</td>
<td>-</td>
<td>137</td>
<td>0.278</td>
<td>13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>suspended</td>
<td>0</td>
<td>63.0</td>
<td>0.215</td>
<td>16.0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>used</td>
<td>85</td>
<td>12.7</td>
<td>32.9</td>
<td>0.133</td>
<td>22.2</td>
<td>27.6</td>
</tr>
</tbody>
</table>

7.6 The effect of the process conditions

In addition to the effect of the montmorillonite type, the effect of the process conditions on the deactivation was investigated. In the following sub-paragraphs the effect of the temperature, the water concentration and the solvent type will be discussed.

7.6.1 Temperature

The deactivation of Supreme FF during the conversion of HPOD is affected by the temperature to a minor degree, see Table 7.111. The results from the conversion at 323 K cannot completely be compared, because only \(\pm 80\)% of the HPOD was converted after a batch time of 25 ks, when the catalyst properties were determined. The temperature effect is most evident for \(\Phi\), which value increases from 2.9% to 13.3% in the temperature range from 323 to 383 K, after the conversion of HPOD under comparable conditions. This indicates that the deposition rate proceeds with a lower activation energy than the conversion. The physical properties do not quantitatively follow this effect, but qualitatively a trend is observed towards higher
Table 7.11 Supreme FF properties after complete conversion of HPOD ($C_0 = 30 \text{ mol m}^{-3}$) of batch I with 5 kg m$^{-3}$ Supreme FF in MGT-oil at varying temperatures.

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>Batch time [ks]</th>
<th>$C_C$ [w/w%]</th>
<th>$A_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>$V_{pore}$ [cm$^3$ g$^{-1}$]</th>
<th>$d_{pore}$ [nm]</th>
<th>$\Phi$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>323.15*</td>
<td>25</td>
<td>17.1</td>
<td>26.0</td>
<td>0.054</td>
<td>9.5</td>
<td>2.9</td>
</tr>
<tr>
<td>343.15</td>
<td>100</td>
<td>18.2</td>
<td>23.9</td>
<td>0.051</td>
<td>11.3</td>
<td>3.6</td>
</tr>
<tr>
<td>363.15</td>
<td>80</td>
<td>17.4</td>
<td>27.1</td>
<td>0.078</td>
<td>10.6</td>
<td>6.4</td>
</tr>
<tr>
<td>383.15</td>
<td>25</td>
<td>16.3</td>
<td>31.9</td>
<td>0.092</td>
<td>10.2</td>
<td>13.3</td>
</tr>
</tbody>
</table>

* Only 80% conversion was achieved after 25 ks

BET surface areas and larger pore volumes at higher temperatures. Under the conditions of Table 7.111 furthermore ±90% deactivation has taken place, causing low BET surface areas and values for $\Phi$ with relatively large errors. This explains the fact that the linear relationship between the BET surface area and the deactivation function is not evident.

7.6.2 Water concentration

A more significant effect on $\Phi$ was observed for the water concentration, see Table 7.14. By increasing the water concentration from 15 to 120 mol m$^{-3}$, the value of the deactivation function increased from 7.4 to 31.6% after the conversion of HPOD from batch II with an initial concentration of 30 mol m$^{-3}$ at 363 K in MCT-oil. The physical parameters clearly show the same trend, although the BET surface area of the catalyst used at a water concentration of 120 mol m$^{-3}$ is somewhat lower than expected from the deactivation function.

Table 7.14 Supreme FF properties after complete conversion HPOD ($C_0 = 30 \text{ mol m}^{-3}$) from batch II with 5 kg m$^{-3}$ Supreme FF at 363 K in MCT-oil at varying water concentrations.

<table>
<thead>
<tr>
<th>$C_{H_2O}$ [mol m$^{-3}$]</th>
<th>Batch time [ks]</th>
<th>$C_C$ [w/w%]</th>
<th>$A_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>$V_{pore}$ [cm$^3$ g$^{-1}$]</th>
<th>$d_{pore}$ [nm]</th>
<th>$\Phi$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>80</td>
<td>17.4</td>
<td>26.8</td>
<td>0.073</td>
<td>12.8</td>
<td>7.4</td>
</tr>
<tr>
<td>35</td>
<td>80</td>
<td>17.1</td>
<td>41.2</td>
<td>0.090</td>
<td>11.5</td>
<td>12.5</td>
</tr>
<tr>
<td>120</td>
<td>80</td>
<td>15.9</td>
<td>51.7</td>
<td>0.128</td>
<td>10.8</td>
<td>31.6</td>
</tr>
</tbody>
</table>

An explanation for this phenomenon is that at higher water concentrations, which consequently leads to more adsorbed water on the catalyst surface, the acidity of the surface weakens. If the deposition rate is related to the acidity, less deactivation at higher water concentrations would be observed. Another explanation is that higher concentrations of water inhibit condensation reactions, which may be a type of reaction responsible for the deposition of coke material.
The effect of the solvent on the deactivation function was even more pronounced, see Table 7.V. While the deactivation in MCT-oil and apolar solvents such as toluene and decane resulted in a value of the deactivation function of less than 15% after complete conversion of 30 mol m$^{-3}$ HPOD at 363 K by 5 kg m$^{-3}$ Supreme FF, the value for the deactivation function was much higher in ethyl octanoate and almost no deactivation had occurred in 1-butanol. Therefore the deactivation function appears to be related to the polarity of the solvent in which the reaction is carried out. Whereas by mere suspending of Supreme FF in MCT-oil, the BET surface area was decreased by ±35%, this did not occur in the other solvents. This may explain the difference in the deactivation function between the conversion in MCT-oil and ethyl octanoate, which show a comparable polarity and for which therefore comparable degrees of deactivation were expected. The fact that a large part of the increase in the carbon content and the decrease in the BET surface area in MCT-oil is attributed to the solvent furthermore suggests that the deposition rate related to the reaction components is higher in decane and toluene than in MCT-oil.

The deactivation function after complete conversion again corresponds very well to the physical properties of the catalysts, although the BET surface area found after the conversion in ethyl octanoate is low with respect to the deactivation function. The data furthermore indicate that the degree of deactivation in decane is very extreme with 21.8% (w/w) of coke deposited and a value for the deactivation function of only 2%. In contrast to that the conversion in 1-butanol only led to 1.6% of coke, while the BET surface area and the deactivation function remained higher than 85%.

Table 7.V Supreme FF properties after complete conversion HPOD (Co = 30 mol m$^{-3}$) from batch II (in 1-butanol from batch I) with 5 kg m$^{-3}$ Supreme FF at 363 K in varying solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Batch time [ks]</th>
<th>$C_C$ [w/w%]</th>
<th>$A_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>$V_{pore}$ [cm$^3$ g$^{-1}$]</th>
<th>$d_{pore}$ [nm]</th>
<th>$\Phi$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decane</td>
<td>25</td>
<td>21.8</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>2.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>25</td>
<td>16.2</td>
<td>43.6</td>
<td>0.105</td>
<td>9.6</td>
<td>14.8</td>
</tr>
<tr>
<td>MCT</td>
<td>80</td>
<td>17.1</td>
<td>41.2</td>
<td>0.090</td>
<td>11.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Ethyl octanoate</td>
<td>25</td>
<td>11.4</td>
<td>124.4</td>
<td>0.209</td>
<td>6.7</td>
<td>77.9</td>
</tr>
<tr>
<td>1-butanol</td>
<td>25</td>
<td>1.6</td>
<td>275.9</td>
<td>0.392</td>
<td>5.7</td>
<td>93.4</td>
</tr>
</tbody>
</table>

* Not measured

For this dramatic effect of the solvent, the same explanations as given for the effect of the water concentration can be advanced. Since it is known that more polar solvents weaken the acid strength of montmorillonites (Solomon, 1971; Adams et al., 1983), a lower acidity may diminish the rate of deposition. The material potentially responsible for the deactivation may also be prevented from deposition due to strong adsorption of the polar solvents, such as 1-butanol, on the catalyst surface.
7.7 Modelling of the deactivation

7.7.1 Introduction

This paragraph describes the development of a simple model and the determination of its kinetic parameters by regression of the deactivation described in this chapter. In order to determine the deactivation kinetics separately from the intrinsic kinetics of the main reaction, the principle of separable kinetics, introduced by Szepe and Levenspiel (1971), was applied:

\[ r = r_0 \text{ (present conditions)} \Phi \text{ (past history)} \] (7.4)

in which the rate at which the deactivation function decreases with time is only a function of the present conditions:

\[ \frac{d\Phi}{dt} = -f \text{ (present conditions)} \] (7.5)

Although it has been shown that the assumption of separability is not always valid (Löwe and Tanger, 1987), the separability is still commonly applied (Butt, 1984), because of its simplicity.

7.7.2 Model description

In paragraph 7.4 it was concluded that the hydroperoxide or other components preceding the rate determining step, were involved in the deactivation. This parallel deactivation in its most simplified form can be written as:

HPOD $\rightarrow$ Products

HPOD $\rightarrow$ Poison\$

(7.1) (7.11)

In paragraph 7.4 the following linear relationship between the deactivation function $\Phi$ and the BET surface area $A_{\text{BET}}$ had been demonstrated:

\[ \Phi = -15.5 + 0.565 A_{\text{BET}} \] (7.6)

This relation allows the BET surface area to be used as activity parameter. By using the BET surface area as activity parameter a more physical representation of the deactivation is obtained than by using the deactivation function $\Phi$, which has no further physical meaning.
The deactivation could best be described with the following rate equations, which are based on the equations given by Levenspiel (1972) for parallel deactivation:

\[ \frac{dC_{HPOD}}{dt} = -k_1 C_{HPOD} C_{cat} \Phi \]  
(7.7)

\[ \frac{dA_{BET}}{dt} = -k_2 C_{HPOD} \Phi^2 \]  
(7.8)

with the following initial conditions at \( t=0 \):

\[ C_{HPOD} = C_{HPOD,0} \]  
(7.9)

\[ \Phi = 1 \]  
(7.10)

\[ A_{BET} = 206 \, \text{m}^2 \, \text{g}^{-1} \]  
(7.11)

Via Equation 7.6 the parameters \( \Phi \) and \( A_{BET} \) are exchangeable in Equations 7.7 and 7.8 and as a consequence Equations 7.10 and 7.11 refer to the same initial condition. The equations indicate that the conversion of HPOD is first order with respect to HPOD and linearly related to the catalytic activity \( \Phi \). The decrease of the deactivation function and hence the BET surface area could best be described by Equation 7.8. The deactivation appeared to be first order with respect to HPOD and second order with respect to \( \Phi \). This can be visualised by the idea that for the deactivation of one site, two active sites are needed.

### 7.7.3 Modelling results

The kinetic parameters of Equations 7.7 and 7.8 were determined by regression with a Marquardt routine (Marquardt, 1963) with the HPOD concentration being the single response. The BET surface area could not be used as response due to the limited amount of data. The set of data that was used for this regression consisted of 24 experiments, each consisting of \( \pm 8 \) time sampling points, in the range shown in Table 7.VI. The experiments carried out in MCT with Supreme FF as catalyst for the conversion of the hydroperoxide from batch I were used. This batch was studied under a broader range of experimental conditions.

<table>
<thead>
<tr>
<th>Process condition</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [K]</td>
<td>323 - 383</td>
</tr>
<tr>
<td>( C_{HPOD,0} ) [mol m(^{-3})]</td>
<td>6 - 60</td>
</tr>
<tr>
<td>( C_{cat} ) [kg m(^{-3})]</td>
<td>2.5 - 10</td>
</tr>
</tbody>
</table>

The final kinetic parameter estimates with their corresponding 95% confidence intervals are shown in Table 7.VII. The \( F \)-value of the regression amounted to 11400. The value of the largest binary correlation coefficient was 0.97. From the \( F \)-
Table 7.VII Kinetic parameter estimates with their corresponding 95% confidence intervals for the estimates from a regression of 24 experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1^*$</td>
<td>mol kg$^{-1}$ s$^{-1}$</td>
<td>$1.5 \pm 0.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$A_2^*$</td>
<td>-</td>
<td>$1.5 \pm 0.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>$E_{act,1}$</td>
<td>kJ mol$^{-1}$</td>
<td>$52 \pm 5$</td>
</tr>
<tr>
<td>$E_{act,2}$</td>
<td>kJ mol$^{-1}$</td>
<td>$38 \pm 8$</td>
</tr>
</tbody>
</table>

of a regression result, in which the evolution of $\Phi$ vs. batch time is also shown. It is clear that initially, when high concentrations of HPOD are present, the deactivation function decreases very fast, while at longer batch times this decrease is much slower.

Figure 7.8 shows the result of the regression for the conversions at different temperatures. A very good description of the disappearance curves by Equations 7.7 - 7.11 with the parameters in Figure 7.9 is obtained over the applied temperature range. The apparent activation energy for the conversion of the hydroperoxide amounts to 52 kJ mol$^{-1}$, which is low compared to other reactions catalysed by montmorillonites (McCabe, 1992) and especially compared to the activation energy for the conversion of cumene hydroperoxide, described in chapter 4, for which an activation energy of 105 kJ mol$^{-1}$ was calculated by regression. This may be explained by a different rate determining step. In this paragraph only global parameters are estimated, and therefore no information about the rate determining value, the confidence intervals, the calculated disappearance curves, see Figure 7.1, Figure 7.2 and Figure 7.5 and the parity plot, see Figure 7.8, it can be concluded that an adequate description of the deactivation is obtained. This adequate description can be seen as a indication that the assumption of the separated kinetics is justified. In Figure 7.9 another example is given.

Figure 7.8 Calculated vs. experimental HPOD concentrations. Calculated by Equations 7.7 - 7.11 with the parameters from Table 7.VII.
The montmorillonite catalysed conversion of hydroperoxides

Figure 7.9 HPOD concentration (1) and $\Phi$ (2) vs. batch time during the Supreme FF (5 kg m$^{-3}$) catalysed conversion at 363 K in MCT-oil. Markers: experimental data points, curves: calculated by Equations 7.7 - 7.11 and with the parameters reported in Table 7.VII

Figure 7.10 HPOD concentration vs. batch time during Supreme FF (5 kg m$^{-3}$) catalysed conversion at different temperatures. Markers: experimental data points, curves: calculated by Equations 7.7 - 7.11 and with the parameters reported in Table 7.VII.

step was obtained. The activation energy for the deactivation, see Equation 7.8, was estimated at 38 kJ mol$^{-1}$. Because this is lower than the activation energy for the hydroperoxide disappearance, the deactivation becomes relatively less important at higher temperatures. This confirms the conclusion from paragraph 7.6.1.

7.8 Conclusions

In this chapter it has been shown that during the montmorillonite catalysed conversion of hydroperoxyoctadecadienoic acid an extreme deactivation occurs, resulting, under standard conditions, in a decrease of 90% of the original catalytic activity. This deactivation originates from parallel deactivation, in which the hydroperoxide rather than the reaction products are involved. Carbonaceous material is deposited by which the catalyst pores are filled and blocked and the BET surface area decreases. The smallest pores are blocked first. During deactivation a linear relationship exists between the deactivation function $\Phi$ and the BET surface area. The catalytic active sites are homogeneously distributed over the pores of a catalyst particle with respect to the acid strength and the location. The material responsible for the deactivation is not much dehydrogenated, when compared to the hydroperoxide reactant. The degree of dehydrogenation is independent of the degree of deactivation.

Montmorillonites with comparable acid strengths deactivate to comparable degrees, while the montmorillonites with lower acid strengths show a more varied behaviour. Higher temperatures led to a relatively slower decrease of the deactivation function. A higher water concentration and especially more polar solvents inhibited the deactivation. A decrease in the deposition rate caused by a decrease in the acidity,
or less deposition of deactivating material due to the coverage of the surface by water and polar solvents are explanations for this phenomenon. A simple model has been developed to describe the deactivation. It appeared that the conversion was best described by a first order in the hydroperoxide and the catalyst concentration. The deactivation could best be described by a first order in the hydroperoxide and a second order in the deactivation function. By regression of the experimental data, activation energies of 52 and 38 kJ mol⁻¹ were obtained for the hydroperoxide disappearance rate and the deactivation rate.

References

The montmorillonite catalysed conversion of hydroperoxides
THE MONTMORILLONITE CATALYSED CONVERSION OF 13-HYDROPEROXY-9-CIS,11-TRANS-OCTADECADIENOIC ACID

8.1 Introduction

Hydroperoxides are undesired components in refined oils, since they are important precursors for the formation of flavour components, such as aldehydes and ketones, which cause the oil to become rancid (Frankel 1980, 1984). During refining these hydroperoxides are removed catalytically by treatment with a bleaching earth. Bleaching earths are (acid activated) clay minerals of the montmorillonite type, and represent a certain acidity, responsible for the catalytic properties of the bleaching earth. Although bleaching of oils is performed on a very large scale little is known about the catalytic and chemical reactions, involving hydroperoxides, taking place. As a consequence little is known about the products remaining in the oil after conversion of hydroperoxides during bleaching. Only studies towards the formation of monocarbonyl products during the catalysed conversion of hydroperoxides (Kimoto et al., 1974) have appeared.

In Chapter 7 the deactivation of montmorillonites has been discussed under different conditions, in particular with respect to the disappearance rate of the hydroperoxide. This chapter describes the results of studies towards the reaction network of the montmorillonite catalysed conversion of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid in MCT-oil, see paragraph 8.2. The effect of the montmorillonite type on this network is discussed in paragraph 8.3. The results of
studying the effect of the process conditions, such as the temperature, the water concentration and the solvent will be presented in paragraph 8.4.

8.2 Construction of the reaction network

The main reaction products of the montmorillonite catalysed conversion of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid (13-c,t-HPOD) are listed in Figure 8.1. These components were identified according to the procedure described in paragraph 5.6. Analysis of the formation and selectivities of these components during montmorillonite catalysis as a function of batch time and conversion and identification of volatiles allowed to construct the reaction network, which will be described below.

Based on the information obtained and outlined in this paragraph the reaction network for the montmorillonite catalysed conversion of 13-c,t-HPOD is constructed, which is shown in Figure 8.2. The range of products varies from cleaved components via components in which the C_{18}-chain is maintained, both groups of which the major part could be quantified, to oligomeric products. In this network the presence of intermediates plays a central role, as the majority of the products is formed via these components. The presence, the mechanism of their formation and the evolution of the different reaction components will be discussed in the following.
Chapter 8  

The montmorillonite catalysed conversion of 13-hydroperoxy-9-cis,11-trans-

\( 13\)-c,t-HPOD

![Diagram of proposed reaction network](image)

**Figure 8.2** Proposed reaction network for montmorillonite catalysed conversion of 13-c,t-HPOD with initial selectivities for Supreme FF catalysed conversion at 363 K in MCT-oil.

Numbers with respect to concentrations and selectivities concern the conversion of 31.2 mol m\(^{-3}\) HPOD by 5 kg m\(^{-3}\) Supreme FF at 363 K in MCT-oil.

**Intermediates**

The most remarkable observation in the results of the montmorillonite catalysed conversion of HPOD is that the majority of the products is formed via intermediates. The first indications for this phenomenon were the increase in the product concentrations after the period in which HPOD had completely been converted, see Figure 8.4 and Figure 8.6. It is further clarified by the graphs in which the selectivities towards the products are plotted against the conversion, see Figure 8.7. A very strong increase is observed, which may for a small part be explained by adsorption of the reactants and the products on the montmorillonite surface, leading to a delay in the detection of the products.

![Proposed structures for identity of intermediates](image)

**Figure 8.3** Proposed structures for identity of intermediates.
The montmorillonite catalysed conversion of hydroperoxides

Figure 8.4 Concentration vs. batch time for main reaction components during Supreme FF catalysed conversion of 13-c,t-HPOD at 363 K in MCT-oil.

The major contribution to this phenomenon however must be attributed to the presence of intermediates in the reaction paths, which are converted at a larger time scale than the conversion of HPOD and yield the same products. Determination of the difference between the initial and final selectivities towards the identified products as depicted in Figure 8.7 leads to the conclusion that more of the products is formed via the intermediates than as primary products and that at least 43% of the conversion proceeds via these intermediates.

The intermediates are most probably peroxidic linked dimers, see Figure 8.3. This would explain the formation of the same products from the intermediates and HPOD, since upon protonation the same ionic species originate. It also explains the fact that no contribution to the PV was found, because no hydroperoxide groups are present. The explanation is furthermore substantiated by the analogy with the conversion of cumene hydroperoxide, which also partly proceeds via peroxidic linked dimers, see chapter 4.

Another explanation for the formation of the same products from the intermediates and HPOD is that the intermediates are converted via the hydroperoxides, i.e. that the formation of the intermediates is reversible. Although this may occur to some degree, not all intermediates are converted via the hydroperoxides,

Figure 8.5 Total and linoleic acid hydroperoxide concentrations vs. batch time during the Supreme FF (5 kg m⁻³) catalysed conversion of 13-c,t-HPOD.
since in that case at every point during the experiment the same ratio of the products is expected to be formed.

Hydroperoxyoctadecadienoic acids (HPOD)
In Figure 8.4 the evolution of the main reaction components vs. batch time is shown for the Supreme FF catalysed conversion. The total concentration of the individual isomers of the components is depicted. At a temperature of 363 K, HPOD is converted within 2 ks. The disappearance of HPOD could not be described by a simple rate equation. This is explained by the extreme deactivation of the catalyst, a phenomenon on which has been focused in chapter 7.

During the conversion, the total concentration of all hydroperoxides becomes higher than the concentration of HPOD, as shown in Figure 8.5. Therefore other hydroperoxides than HPOD are being formed during the conversion. These hydroperoxides may for example appear in the form of dihydroperoxides or dimers containing hydroperoxy groups.

Figure 8.6 Concentration vs. batch time for individual isomers of main components and minor and unidentified components during Supreme FF (5 kg m$^{-3}$) catalysed conversion of 13-cis-11-trans-HPOD at 363 K in MCT-oil. a HPOD isomers, b OOD isomers, c thermal cleavage products, d components U1 - U4.
In Figure 8.6.a the evolution of the individual isomers of HPOD is depicted. No isomerisation between the isomers was observed at the time scale of the experiment. This was concluded from the comparable disappearance rates of these isomers, see Figure 8.6.a, and knowing that the HPOD composition is far from thermodynamic equilibrium. Apparently, the isomerisation of the hydroperoxides as evidenced by Chan et al. (1979) does not proceed fast enough to become significant under the conditions employed. The different conversion rates for the cis,trans- and the trans,trans-isomers as found by Tokita and Morita (1985) during the hydrochloric acid catalysed conversion were not observed for the montmorillonite catalysed conversion.

Hock cleavage: hexanal and 12-oxo-10-trans-dodecenoic acid (ODE)
The main products are hexanal and 12-oxo-10-trans-dodecenoic acid (ODE), see Figure 8.4, which are formed simultaneously by the Hock mechanism, as shown in Figure 2.17 (Hock and Lang, 1944; Frankel et al., 1984). The initial selectivities towards hexanal and ODE are 20 and 7 %, whereas the final selectivities, i.e. including the route via the intermediates, amount to 44 and 35%, see Figure 8.7.a.

![Figure 8.7 Selectivity vs. conversion for reaction products of Supreme FF (5 kg m⁻³) catalysed conversion of 13-c,t-HPOD at 363 K in MCT-oil. a OT, ODE and hexanal, b OOD isomers, c DD and OTD isomers, d Components U1 - U4.](image-url)
The Hock-cleavage had already been proven to be a major pathway in model systems in which the Lewis acid catalysed (Gardner and Plattner, 1984), or Brønsted acid catalysed, (Grosch, 1981), conversion of HPOD in apolar solvents was investigated. The results presented here show that the Hock-cleavage also is an important pathway in the montmorillonite catalysed conversion in more practical oils. The fact that higher concentrations of hexanal than ODE are found may be explained by several factors. The isomerisation of the 9-cis to the 10-trans-isomer may not have proceeded completely, both these components may adsorb stronger on the catalyst surface than hexanal, or the former components may have reacted further for example in reactions causing the deactivation.

**Oxooctadecadienoic acids (OOD)**

Other important products appeared to be the oxooctadecadienoic acids (OOD), see Figure 8.4. These components are formed by a loss of water from HPOD. The initial selectivity of 2.8% increases to 10.8% after complete conversion, if the total concentration of the four OOD isomers is considered, see Figure 8.6.b. This increase is again attributed to the intermediates via which the major part is formed.

Figure 8.6.b. indicates that all isomers, i.e. both the cis,trans- and trans,trans- and the positional 9- and 13-oxo-isomers are formed in significant amounts. From Figure 8.6.b it can furthermore be concluded that although the initial selectivities are again much lower than the final selectivities, all isomers already appear as primary products. Especially the formation of the 9-OOD isomers is remarkable and cannot be explained by the presence of the small amount of the 9-HPOD isomers in the

---

**Figure 8.8** Acid catalysed mechanism proposed for the formation of OOD from HPOD.
feed mixture, since the 9-OOD isomers contribute to at least 20% of the OOD isomers, whereas only ±5% of 9-HPOD was present in the feed mixture. Therefore it is clear that the OOD isomers are formed by a mechanism, which does not retain the original isomeric configuration. A thermodynamic distribution however is not completely obtained, since in that case equal amounts of the 9- and 13-OOD isomers and more trans,trans- than cis,trans-isomers would have been observed. A mechanism, which explains the observations is presented in Figure 8.8.

In this mechanism water is released after protonation, resulting in the formation of a positively charged allylic epoxide ion. By deprotonation and rearrangement of the electrons both the cis,trans and trans,trans-isomers can be formed. To enable the formation of the positional isomers an equilibrium is suggested in which to the allylic epoxide ion water is added. Via a proton transfer, an allylic dihydroxide ion may originate with two resonance structures. The reverse of this process from these resonance structures may yield both the 9,10-epoxide and the 12,13-epoxide ions. Release of a proton finally results in the formation of both the 9-oxo- and 13-oxo-isomers.

At higher conversions, the selectivity to the trans,trans-isomers clearly becomes higher than to the cis,trans-isomers, see Figure 8.7.b. This is explained by isomerisation of the cis,trans- to the thermodynamically favoured trans,trans-isomers. Isomerisation can occur due to the presence of the keto-enol equilibrium, which is furthermore catalysed by acids, see Figure 8.9. Once the enol, i.e. the middle structure, has been formed, it may yield both the cis,trans- and trans-trans-isomers upon reformation of the keto component. This process will finally result in a thermodynamic distribution.

\[
\begin{align*}
13\text{-c,t-OOD} & \quad \overset{H^+}{\leftrightarrow} \quad 13\text{-t,t-OOD} \\
& \quad \overset{H^+}{\leftrightarrow} \\
\end{align*}
\]

Figure 8.9 Keto-enol isomerisation responsible for cis-trans isomerisation of oxooctadecadienoic acid.

**Octadecatrienoic acid (OT)**

Octadecatrienoic acids (OT) are formed with an initial selectivity of 2.0%, increasing finally to 4.1%, see Figure 8.7.a. Their formation may partly be explained by the dehydration of HOD, which is present to a small degree in the feed mixture. This however cannot explain all OT, since more of the latter is formed than the amount of HOD originally present. An additional explanation is the formation of HOD from HPOD, followed by fast dehydration of the HOD, as proposed by Yurawecz et al. (1993). More likely however, the remaining part has been formed by cleavage of hydrogen peroxide as shown in Figure 8.10. This process has also been observed for the acid catalysed decomposition of aryl hydroperoxides by Bissing et al. (1964).
During both the dehydration of HOD and the cleavage of hydrogen peroxide from HPOD a pentadienylic ion is formed, from which both 9,11,13- and 8,10,12-OT may be formed, between which no distinction could be made.

\[
\begin{align*}
13\text{-c,t-HOD} & \quad \xrightarrow{+ H^+} \quad 13\text{-c,t-HPOD} \\
R_1 & \quad \longrightarrow & \quad R_1 & \quad \longrightarrow \\
\quad \xrightarrow{- H_2O} & \quad \xrightarrow{- H_2O_2} \\
R_2 & \quad \longrightarrow & \quad R_2 & \\
\quad \xrightarrow{- H^+} & \quad \\
R_3 & \quad \longrightarrow & \quad R_3 & \\
\end{align*}
\]

Figure 8.10 Mechanisms proposed for the formation of octadecatrienoic acids.

Thermal products

Next to products, for which acid catalysed mechanisms are held responsible, also products were found which are suggested to be formed by competitive thermally induced reactions, i.e. decadienal (DD) and oxotridecadienoic acids (OTD). Therefore they do not appear in the acid catalysed network shown in Figure 8.2. These components are formed with selectivities lower than 1%, see Figure 8.7. In chapter 6 the thermal reactions have already been discussed in detail. Interesting to note however, under the montmorillonite catalysed conditions these products are predominantly formed via intermediates, indicated by an increase in the selectivities vs. conversion, see Figure 8.7.c. This increase is for OTD even more pronounced than for the acid catalysed products discussed so far. This strong increase suggests that the intermediates are more stable towards thermally induced reactions than HPOD, but when they are converted by thermally induced mechanisms, they yield the same products as HPOD.

The 13-c,t-OTD isomer appeared to be the main isomer until 100% conversion, which is in contrast to the thermal conversion described in the previous chapter. This discrepancy may be explained by a difference in reaction conditions. The temperature for example is 30 K lower than applied during the thermal conversion. Furthermore isomerisation between the cis,trans- and trans,trans-isomers of OTD occurred, deduced from the simultaneous increase in the trans,trans- and decrease of the cis,trans-isomer after reaction times of 1500 s, see Figure 8.7.c. This isomerisation appears to be acid catalysed since it occurs much faster under these conditions than under the thermal conditions described in paragraph 6.2. The keto-enol equilibrium, which was already suggested to be responsible for the isomerisation of OOD isomers, provides an adequate explanation for this phenomenon. Because the total concentration OTD decreases in the final stages of the reaction, these components are furthermore subject to consecutive reactions.
Volatile reaction products

The volatile components formed after Supreme FF (5 kg m\(^{-3}\)) catalysed conversion of 13-c,t-HPOD during 80 ks at 363 K in MCT-oil were identified and quantified, according to the method of Turksma, see paragraph 5.4, resulting in the data shown in Table 8.1. Hexanal is the main volatile as expected from the Hock mechanism. The value of 12.6 mol m\(^{-3}\) found with this method is in good agreement with the value of 13.7 mol m\(^{-3}\) found with the purge-and-trap technique. 2-trans-nonenal is the corresponding product from 9-HPOD and is also formed in significant amounts, 0.58 mol m\(^{-3}\). These results are furthermore in reasonable agreement with the studies of Kimoto and Gaddis (1969) in which 32% conversion to hexanal and 2-trans-nonenal was found. The results presented here account for 40% conversion according to the Hock cleavage. Although in the studies of Kimoto and Gaddis equal mixtures of 9- and 13-HPOD were involved, much more hexanal than 2-trans-nonenal was found. In contrast to that result, from the data from Table 8.1 a ratio 2-trans-nonenal to hexanal of 0.046 was calculated, which is comparable to the ratio 9- to 13-HPOD of 0.052 involved. This indicates that in this investigation the Hock cleavage occurs to the same degree for both positional hydroperoxide isomers and that prior to cleavage no isomerisation of the hydroperoxides takes place.

Table 8.1 Concentration of volatile products in mmol m\(^{-3}\) after Supreme FF catalysed (5 kg m\(^{-3}\)) conversion of 13-c,t-HPOD (31.2 mol m\(^{-3}\)) at 363 K in MCT-oil.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (mmol m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pantanal</td>
<td>83.5</td>
</tr>
<tr>
<td>2-Heptanone</td>
<td>9.7</td>
</tr>
<tr>
<td>Hexanal</td>
<td>12600</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>41.6</td>
</tr>
<tr>
<td>Heptanal</td>
<td>84.8</td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>0</td>
</tr>
<tr>
<td>Octanal</td>
<td>59.2</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0</td>
</tr>
<tr>
<td>Nonanal</td>
<td>90.7</td>
</tr>
<tr>
<td>Butanoic acid</td>
<td>3.5</td>
</tr>
<tr>
<td>t2-Heptenal</td>
<td>50.7</td>
</tr>
<tr>
<td>Pentanoic acid</td>
<td>20</td>
</tr>
<tr>
<td>t2-Octenal</td>
<td>129</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>1580</td>
</tr>
<tr>
<td>t2-Nonenal</td>
<td>583</td>
</tr>
<tr>
<td>Heptanoic acid</td>
<td>17.2</td>
</tr>
<tr>
<td>t2-Decenal</td>
<td>54.5</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>223</td>
</tr>
<tr>
<td>t2,c4-Decadienal</td>
<td>11.1</td>
</tr>
<tr>
<td>t2,t4-Decadienal</td>
<td>40.7</td>
</tr>
</tbody>
</table>

Other (unsaturated) aldehydes also are important volatiles. The decadienals, formed by a thermally induced mechanism, are found in amounts (52 mmol m\(^{-3}\)) in good agreement with the HPLC-UV analysis results (60 mmol m\(^{-3}\)). The presence of 2-trans-octenal and octanoic acid can also be explained by thermally induced mechanisms, but the formation of the other components is less evident from a mechanistic point of view.
Unidentified components
The selectivity towards the four components U1 - U4 amounts to 9.2% at 100% conversion, see Figure 8.7.d, based on estimated molar absorbencies discussed in paragraph 5.7. This number indicates that these components constitute a significant part of the reaction products. In paragraph 5.6.3 possible identities for these components were discussed and other isomers of OOD were suggested. In addition, components U1 - U4 displayed a similar behaviour to OOD, with respect to the evolution of their concentration and selectivities vs. batch time and conversion, see Figure 8.6 and Figure 8.7. An explanation for the formation of other, double rather than triple conjugated, OOD may be advanced based on the mechanism shown in Figure 8.8. In this mechanism water is suggested to add to the positively charged allylic epoxide ion on the outer 9- and 13-positions. This may however also occur on the middle 11-position, leading to double conjugated OOD isomers.

Conclusions
The total initial selectivity towards identified reaction products of the montmorillonite catalysed conversion of HPOO by Supreme FF at 363 K in MCT-oil amounts to 16.8%, and including components U1 - U4 19.8%. This indicates that the identity of at least 80% of the primary products is not elucidated. At 100% conversion 38.0% of the products is identified, while at even longer reaction times this figure increases to at least 53.5%; and including components U1 - U4 to 47.5 and 62.7%. To the latter value 4% can be added, due to the formation of other volatiles than hexanal. Furthermore 8% (w/w) of the HPOO feed is involved in the process of deactivation, see Chapter 7. These data close the carbon balance for ±75%, higher than any study prior to the present one has achieved.

By subtracting the total initial selectivity of 19.8% from the final selectivity of 62.7%, it is deduced that about 43% of the identified products is formed via intermediates and thus that the initial selectivity towards the intermediates must be higher than 43%, neglecting the previously discussed adsorption and desorption effects.

The epoxyhydroxy- and trihydroxyoctadecenoic acids observed by Gardner et al. (1984a,b) during the Brønsted acid catalysed conversion in aqueous solvents were not observed during the montmorillonite catalysed conversion. On the contrary, it is very unlikely for these products to originate, since montmorillonites have powerful dehydrating properties for alcoholic components.

8.3 The effect of the montmorillonite type
Next to Supreme FF several other montmorillonite type catalysts have been used for the conversion of HPOD. The characteristics of these montmorillonites are shown in Table 5.111. Figure 8.11 shows the hydroperoxide concentration vs. batch time for these different catalysts. From this Figure it follows that the montmorillonites with the highest acid strength, Supreme FF, XJ-9126 and F-20, show the highest activity
The montmorillonite catalysed conversion of hydroperoxides

Figure 8.11 HPOD concentration vs. batch time with different types of catalysts, 10 kg m\(^{-3}\) in MCT-oil at 363 K.

towards the HPOD conversion. The activity of the moderately activated ACC FF is much lower, whereas the lowest activity is observed for the non-activated B-80, which possesses a relatively high natural activity. These observations indicate that the reaction rate is related to the degree of activation of the montmorillonite surface, i.e. to the acidity of the catalyst. This was also the conclusion from the studies performed by Boki et al. (1989). Although the BET surface area of ACC FF and B-80 is two to three times as low, this does not explain their lower activity, which is two to three orders of magnitude lower compared to the more active catalysts.

The selectivity of the montmorillonite catalysed conversion is also affected by the type of catalyst. This is concluded from Figure 8.12, in which the initial selectivities and the selectivities at 100% conversion of HPOD are depicted for the different montmorillonite types used. The general trend is that higher activated montmorillonites lead to more of the identified products, i.e. more conjugated components. Furthermore for all montmorillonites it is observed that the initial selectivities are lower than the selectivities at 100% conversion, indicating that the occurrence of intermediates is a general phenomenon for this type of catalysis. The differences in the initial selectivities are smaller than in the selectivities at 100% conversion, indicating either less production of intermediates for the less active montmorillonites and more unidentified products, or that the less activated montmorillonites are less able to convert the intermediates once they have been formed.

The differences in the selectivity between the montmorillonites are the most pronounced for the cleavage product ODE, see Figure 8.12.a and c. This selectivity is the highest for XJ-9126 and F-20, followed by resp. Supreme FF, ACC FF and B-80, with values for the selectivity at 100% conversion ranging from 3.8 to 28.7 %.
Figure 8.12: Selectivities of products during montmorillonite catalysed (10 kg m⁻³) conversion of 13-cis,11-trans-HPOD at 363 K in MCT-oil with different montmorillonite types. a initial and c at 100% conversion of OT, ODE and components U1 - U4, b initial and d at 100% conversion of OOD and OTD isomers.

Since the montmorillonites which were less activated yield less of this product, it is concluded that the degree to which the Hock-cleavage occurs is related to the acid strength.

The initial selectivity towards OT is comparable for all montmorillonites with the exception of F-20, which shows a higher initial selectivity. The initial selectivities to the products U1 - U4 are also comparable with the selectivities of ACC FF being a little lower and surprisingly, of B-80 being a little higher. The selectivities to these products at 100% conversion all show the same trend: the values are higher for the higher activated montmorillonites Supreme FF, XJ-9126 and F-20. This may again be explained by the inability of the less activated montmorillonites to convert the intermediates.

The differences in the selectivities towards the OOD isomers are less pronounced, see Figure 8.12.b and d, with Supreme FF resulting in the highest and ACC FF in the lowest selectivity. At 100% conversion the selectivities with the less activated montmorillonites are even more comparable to the higher activated types. This indicates that the mechanism for these products is hardly influenced by the acidity of
The montmorillonite catalysed conversion of hydroperoxides

the catalyst. The 9-OOD isomers however are formed in larger amounts by the higher activated montmorillonites. This suggests that the higher acidity is responsible for the oxygenated group to shift form the 13- to the 9- position. This also appears to be the case to a minor degree for the formation of the trans,trans-isomers compared to the cis,trans-isomers. Remarkable furthermore is the fact that with XJ-9126 no cis,trans-isomers but only trans,trans-isomers are formed.

The OTD isomers are only formed in significant amounts during conversion by ACC FF and B-80, see Figure 8.12.b and d, caused by competition of thermal induced reactions. The OTD isomers have been shown to be major thermal reaction products, see paragraph 6.2 and competition with thermal induced reactions becomes important with these montmorillonite types, since the activity of these types is relatively low, resulting in a higher average HPOO concentration available for these thermal reactions. As during pure thermal conversion, the cis,trans-isomer initially is the main isomer, while the trans,trans-isomer becomes the main isomer in later stages of the reaction, due to isomerisation.

8.4 The effect of the process conditions

Several process conditions have been varied to study their effect on the montmorillonite catalysed conversion. Supreme FF was chosen as the catalyst. By varying the temperature, see paragraph 8.4.1, information about the activation energy was obtained. The water concentration and the solvent type are important parameters for the activity of the montmorillonite. Their effect on the conversion of 13-c,t-HPOO is discussed in paragraphs 8.4.2 and 8.4.3.

8.4.1 Temperature

The temperature for the Supreme FF catalysed conversion of HPOO was varied in the range of 323 - 383 K. The effect of the temperature on the disappearance rate of HPOO has already been discussed with respect to the deactivation, see paragraph 7.6.1. Via the development of a simple kinetic model and subsequent regression of the experimental data the activation energy was determined, which amounted to 53 kJ mol\(^{-1}\).

The selectivity was also studied as a function of temperature. The initial selectivities and the selectivities at 100% conversion are shown in Figure 8.13. Generally it can be concluded from these results that the effect of the temperature on the selectivities is not very pronounced. Another general phenomenon consists of the lower selectivities observed from the conversion of batch II compared to batch I. This can be explained by the conversion of other unstable components present as impurities in the feed mixture.

The differences in the initial selectivity and the selectivity at 100% conversion towards the OOD isomers are larger at lower temperatures. This indicates that at
lower temperatures more of these products is formed via intermediates and at higher temperatures more is formed directly from HPOD. The same feature is observed for OTD and components U1 - U4 while the reverse is observed for ODE.

8.4.2 Water concentration

Since it is known that water generally has a dramatic negative effect on the catalytic activity of montmorillonite minerals (Solomon et al., 1971; Adams et al., 1983), the influence of the water concentration on the Supreme FF catalysed conversion of HPOD was investigated to determine the degree of this influence. The water concentration of 15 mol m\(^{-3}\) was obtained by drying of Supreme FF during 16 hours at 363 K, whereas the concentration of 120 mol m\(^{-3}\) was obtained by addition of water prior to the reaction. This concentration approaches the maximum water concentration soluble in MCT-oil. The water concentration of 35 mol m\(^{-3}\) is the concentration obtained under standard reaction conditions as used throughout this chapter.
The montmorillonite catalysed conversion of hydroperoxides

Figure 8.14 HPOD concentration vs. batch time during Supreme FF (5 kg m⁻³) catalysed conversion at 363 K in MCT-oil at different water concentrations.

In contrast to what was expected, it appeared that the water concentration hardly affected the disappearance rate of HPOD, see Figure 8.14, and even a slight opposite effect was observed. This phenomenon is difficult to explain. It is possible that the deactivation which was more pronounced under drier conditions, see chapter 7, obscures the higher activation of the montmorillonite surface.

The selectivity of the conversion however is significantly affected by the water concentration in the MCT-oil. As examples the selectivities of ODE, OOD, OT and component U2 are depicted as a function of the conversion and the water concentration in Figure 8.15. The selectivities of the other products are tabulated in Table 8.II.

It appeared that the initial selectivity towards many products was higher at lower water concentrations. At the lowest water concentration the selectivity vs. the conversion curves went through a minimum for some of the products. This can be explained by the higher acidity of the montmorillonite under these conditions, being able to directly convert HPOD to these products. This means that less of the products is formed via the intermediates. Still a significant part of the products however is formed via the intermediates as indicated by the sharp increase in the selectivities of the products in the final stages of the reaction. Whereas the initial selectivities are generally the highest under the driest conditions, the selectivities at higher conversions vary as a function of the water concentration.
The selectivity towards ODE for example is during the complete reaction the highest at the lower water concentration of 15 mol m$^{-3}$, see Figure 8.15.a. The selectivities towards OOD (total of four isomers), OT and component U2 however are the highest in the final stages of the reaction at the highest water concentration. Remarkable is that OOD is the product of a dehydration, which is expected to proceed more rapidly under drier conditions. An explanation for this phenomenon is that the intermediate in the formation of these components, see Figure 8.8, is more stable under more humid conditions. If the formation of the intermediate is the rate determining step, the reaction towards OOD becomes more dominant. The same explanation is applicable to the formation of OT with cleavage of hydrogen peroxide.

Furthermore remarkable is the fact that the selectivities to the identified products is generally the lowest at the intermediate water concentration. A possible explanation is that at the low water concentrations the initial acidity of the catalyst is high leading to high initial selectivities in combination with relatively strong deactivation. At the water concentrations of 35 and 120 mol m$^{-3}$ the initial selectivities towards the identified products are comparable. The higher selectivities at 120 mol m$^{-3}$ water in
The montmorillonite catalysed conversion of hydroperoxides

Table 8.11 Selectivities of products as a function of the water concentration during the Supreme FF catalysed (5 kg m⁻³) conversion of 13-c,t-HPOD at 363 K in MCT-oil.

<table>
<thead>
<tr>
<th>Component</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 mol m⁻³ H₂O</td>
</tr>
<tr>
<td></td>
<td>init.</td>
</tr>
<tr>
<td>Total OOD</td>
<td>6.5</td>
</tr>
<tr>
<td>13-c,t-OOD</td>
<td>1.8</td>
</tr>
<tr>
<td>13-t,t-OOD</td>
<td>3.5</td>
</tr>
<tr>
<td>9-t,t-OOD</td>
<td>1.1</td>
</tr>
<tr>
<td>OT</td>
<td>3.3</td>
</tr>
<tr>
<td>Total OTD</td>
<td>0.5</td>
</tr>
<tr>
<td>13-c,t-OTD</td>
<td>0.4</td>
</tr>
<tr>
<td>13-t,t-OTD</td>
<td>0.1</td>
</tr>
<tr>
<td>ODE</td>
<td>27.0</td>
</tr>
<tr>
<td>DD</td>
<td>0.0</td>
</tr>
<tr>
<td>U1</td>
<td>2.1</td>
</tr>
<tr>
<td>U2</td>
<td>6.0</td>
</tr>
<tr>
<td>U3</td>
<td>3.3</td>
</tr>
<tr>
<td>U4</td>
<td>0.9</td>
</tr>
</tbody>
</table>

* After batch time of 80 ks.

The later stages of the reaction may be caused by less deactivation, resulting in more conversion of the intermediates.

8.4.3 Solvent

From the results of Solomon et al. (1971) and Adams et al. (1983) it is known that the type of solvent also affects the activity of montmorillonite catalysts. To determine its effect on the conversion of HPOD, several solvents were employed ranging from apolar such as decane and toluene to more polar solvents such as 1-butanol. In Figure 8.16 the HPOD concentration vs. batch time curves are depicted. It can be concluded that the conversion is the fastest in the more apolar solvents decane and toluene and the lowest in the most polar solvent 1-butanol. This is in agreement with the results of Solomon et al. (1971). The conversion in MCT-oil, having an intermediate polarity takes an intermediate position. The conversion in ethyl octanoate is almost as fast as in toluene and decane, whereas based on its polarity a rate comparable to that in MCT-oil was expected. The lower reaction rate in the more polar solvents can be explained by the dissipating effect of the polar solvents on the proton charge. This leads to a reduced acid strength, corresponding to a lower activity.
The montmorillonite catalysed conversion of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid takes place at a time scale of 2 ks and leads to a complex reaction mixture, although less complex than during thermal conversion. The main products, formed via the Hock cleavage are, 12-oxo-10-trans-dodecenoic acid and hexanal. Other products are oxooctadecadienoic acid isomers, octadecatrienoic acid, oxotridecadienoic acid isomers, which are formed by thermal induced mechanisms and 19 different volatile products. The majority of these products is formed via intermediates, which are more difficult to convert than the hydroperoxide.

8.5 Conclusions

The montmorillonite catalysed conversion of 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid takes place at a time scale of 2 ks and leads to a complex reaction mixture, although less complex than during thermal conversion. The main products, formed via the Hock cleavage are, 12-oxo-10-trans-dodecenoic acid and hexanal. Other products are oxooctadecadienoic acid isomers, octadecatrienoic acid, oxotridecadienoic acid isomers, which are formed by thermal induced mechanisms and 19 different volatile products. The majority of these products is formed via intermediates, which are more difficult to convert than the hydroperoxide.
The montmorillonite catalysed conversion of hydroperoxides

Also other hydroperoxides are formed during the conversion, although these are converted with comparable rates as hydroperoxyoctadecadienoic acid. The identified products account for up to 75% of the carbon balance.

The type of montmorillonite strongly affects the reaction rate. The higher activated the catalyst, the faster the reaction. Furthermore lower selectivities are observed towards the identified products with less activated montmorillonites. This is explained by their inability to convert the intermediates. This phenomenon is most pronounced for the selectivity towards 12-oxo-10-trans-dodecenoic acid and hexanal for which the selectivities at 100% conversion vary between 4 and 29%.

At lower temperatures the conversion proceeds more via the intermediates. In contrast to what is generally observed, the water concentration does not affect the reaction rate. At lower water concentrations less of the identified products is formed via the intermediates. At higher water concentrations more oxooctadecadienoic acid and octadecatrienoic acid is formed, whereas at lower water concentrations more cleavage occurs. More polar solvents inhibit the conversion to some degree, explained by strong adsorption of these solvents, resulting in dissipation of the

<table>
<thead>
<tr>
<th>Product</th>
<th>MCT (I)</th>
<th>Toluene (I)</th>
<th>MCT (II)</th>
<th>Toluene (II)</th>
<th>Ethyl oct (II)</th>
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<tbody>
<tr>
<td>13-ODD</td>
<td>25.5</td>
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<tr>
<td>9-1-ODD</td>
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<tr>
<td>15-ODD</td>
<td>25.5</td>
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<td>13-1-ODD</td>
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<td>15-1-ODD</td>
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<tr>
<td>Total ODD</td>
<td>75.0</td>
<td>25.0</td>
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<tr>
<td>Selectivity [mol %] at 100% conv.</td>
<td>MCT (I)</td>
<td>Toluene (I)</td>
<td>MCT (II)</td>
<td>Toluene (II)</td>
<td>Ethyl oct (II)</td>
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<td>MCT (II)</td>
<td>Toluene (II)</td>
<td>Ethyl oct (II)</td>
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<td>Toluene (I)</td>
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<td>Ethyl oct (II)</td>
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</table>

Figure 8.17 Selectivities of products during the Supreme FF (5 kg m⁻³) catalysed conversion of 13-c,i-HPOD in different solvents. a resp. b initial selectivities and selectivities at 100% conversion of OOD isomers, OT and ODE. c resp. d Same parameters for OTD isomers and components U1 - U4. Between brackets: I: results from batch I, II: results from batch II.
proton charge. The selectivity was less affected by the solvent. The conversion in decane led to less cleavage.

References

- Grosch W., "Model experiments about the formation of volatile carbonyl compounds from fatty acid hydroperoxides" in Schreier P. (Ed.), Flavour '81, Walter de Gruyter, Berlin (1981), 434-448.

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The montmorillonite catalysed conversion of hydroperoxides
GENERAL CONCLUSIONS

The conversion of hydroperoxides by montmorillonites has been studied in order to obtain insight in the kinetics of the complex reaction network of polyunsaturated fatty acid hydroperoxides under refining conditions and especially during bleaching. One linoleic acid hydroperoxide isomer, i.e. 13-hydroperoxy-9-cis,11-trans-octadecadienoic acid (13-c,t-HPOD) was used as reactant to limit this complex network and cumene hydroperoxide was furthermore used as a model compound. Additionally, the thermal conversion of linoleic acid hydroperoxide was investigated.

A literature survey was presented for the chemistry of unsaturated fatty acid hydroperoxides. These components are the primary products of (auto-) oxidation of unsaturated fatty acids and are easily converted. Thermally, radical induced reactions occur, leading to a broad range of products involving volatiles, oxygenated C\textsubscript{18}-components and oligomers. Depending on the conditions, the acid catalysed conversion yields either cleavage products or polyhydroxy C\textsubscript{18}-components. Furthermore an introduction to the characteristics of clay catalysts was given.

The conversion of cumene hydroperoxide towards phenol and acetone catalysed by montmorillonites in addition to its role as model reaction, provides an alternative for the actual process with sulphuric acid as catalyst, which is more difficult to separate from the reaction mixture. A selectivity of 100\% at complete conversion could be obtained with comparable reaction rates. Water strongly inhibited the catalytic activity. Furthermore a so far unknown temporary side-product was observed, which affected the reaction rates due to the simultaneous formation of water. Mechanisms for the formation and decomposition of the side-product were proposed. The conversion of cumene hydroperoxide in the presence of several typical feed stock impurities appeared to be inhibited by 2-phenyl-2-propanol due to competitive adsorption and by the formation of water due to condensation of 2-phenyl-2-
propanol with cumene hydroperoxide. A model, based on Langmuir-Hinshelwood kinetics and consisting of 14 elementary reaction steps, was developed for the reaction network taking place during the conversion of (industrial) cumene hydroperoxide, giving insight in the reaction mechanisms. The parameter estimates, which were all statistically significant and physically reasonable can be applied for reactor design purposes.

The conversion of 13-c,t-HPOD was much more complex. 16 non-volatile reaction components with a chain length of 12 to 18 carbon atoms were identified and quantified. The stereoisomeric configuration of 15 of those components was elucidated. Additionally, 25 volatile products were identified and 21 of them could be quantified. Furthermore, oligomers in the range of 1½ to 3 times the monomer mol mass were detected. During thermal conversion, 14 of these non-volatile and all 25 volatile components were detected, accounting for 13 to 38% of the product carbon balance. The main identified products were components, resulting form cleavage of the C_{18} -chain at either side of the hydroperoxide group, i.e. hexanal and oxotridecadienoic acid. The unsaturated components in the reaction mixture were subject to subsequent polymerisation reactions and for unsaturated o xo-components cis,trans-isomerisation was observed. The apparent activation energy for the thermally induced conversion amounted to 91 kJ mol\(^{-1}\).

The montmorillonite catalysed conversion of 13-c,t-HPOD, in contrast to cumene hydroperoxide, was subject to strong deactivation, typically 80-90% after complete conversion of a batch. The deactivation was attributed to polymerisation of unsaturated reaction components or condensation reactions, resulting in the irreversible deposition of material on the catalyst surface, thereby blocking the pores. The deactivation proceeded by parallel deactivation. During deactivation a linear relation existed between the activity function and the BET surface area. This relation could be applied in a simple model, which was developed to describe the global kinetics of the conversion in the presence of deactivation. The apparent activation energy for the conversion was higher than the apparent activation energy for deactivation, but was twice as low as the activation energy for the conversion of cumene hydroperoxide, attributed to differences in process conditions leading to different reactions or rate determining steps, or due to the fact that for 13-c,t-HPOD an apparent activation energy was determined instead of an activation energy for an elementary step.

During the montmorillonite catalysed conversion of 13-c,t-HPOD, 12 non-volatile and 19 volatile reaction components were observed, accounting for up to 75% of the product carbon balance. The conversion of 13-c,t-HPOD was not only much more complex compared to cumene hydroperoxide regarding the variety of products, it also proceeded under more extreme conditions, i.e. 60 K higher temperatures and 5 times higher catalyst concentrations. Most of the 13-c,t-HPOD products was formed by acid catalysed mechanisms, the main being the Hock mechanism, leading to
hexanal and 12-oxo-10-trans-dodecenoic acid, which is analogous to the conversion of cumene hydroperoxide to phenol and acetone. The majority of the products is formed via intermediates, which converted slower than the hydroperoxides, but yielded the same products. This observation shows similarities with the formation of the ketal side-product and dicumyl peroxide in the reaction network of the conversion of cumene hydroperoxide. Other important products were octadecatrienoic acid, which is analogue to the formation of α-methyl styrene in the cumene hydroperoxide network, and oxooctadecadienoic acids, which are formed by a net dehydration. The observed cis-trans isomerisation of the unsaturated oxo-components was acid catalysed.

The different types of montmorillonites used, showed large differences in activity, attributed to the differences in the acid strength as a consequence of different degrees of activation. F-20 and Supreme FF were the most active catalysts for both reactions. Concerning the conversion of 13-c,t-HPOD, the degree to which the Hock cleavage took place was related to the acidity of the montmorillonite, while the relative degree of deactivation and the ability to convert the intermediates were inversely related to the acidity of the montmorillonite.

In contrast to its effect on the conversion of cumene hydroperoxide, water did not affect the montmorillonite catalysed conversion of 13-c,t-HPOD. This was attributed to compensation of the lower activity by less deactivation at higher water concentrations. Additionally, the 13-c,t-HPOD conversion was also less influenced by the solvent type compared with the cumene hydroperoxide conversion. In the latter case, the global reaction rate increased at least three orders of magnitude from ethanol to heptane. Qualitatively the same trend was followed for both reactions, which was that more polar solvents inhibited the reactions due to stronger adsorption of these solvents, dissipating the proton charge and hence reducing the acid strength. The lower degree of deactivation at higher water concentrations, which much more pronouncedly took place in more polar solvents, was also attributed to this stronger adsorption, preventing material responsible for deactivation from deposition.
The montmorillonite catalysed conversion of hydroperoxides
DANKWOORD

In tegenstelling tot wat de omslag van dit proefschrift doet vermoeden is dit niet het werk van één persoon. Graag wil ik mij tot diegenen waarmee ik het meest intensief heb samengewerkt persoonlijk even richten.

Guy, jouw grote kennis en ervaring zijn van grote waarde geweest voor de inhoud van dit proefschrift. Je wist altijd je vinger op de zere plek te leggen en je kritiek was altijd opbouwend en op zijn plaats.

Ben, jouw enthousiasme en creativiteit waren een stimulans en een aanvulling op mijn werk.

Karel, als één van de initiatoren van het project, enthousiasmeerde je me voor de vetten- en oliëntechnologie. Bovendien wist je de resultaten altijd in zijn perspectief te plaatsen en zorgde je ervoor dat de relevantie niet uit het oog verloren raakte.

Martin, bij jou kon ik altijd terecht met mijn vragen en je maakte het mogelijk gebruik te maken van de technologie en kennis binnen het URL. Je creativiteit en onze stimulerende discussies waren onmisbaar voor het uiteindelijke resultaat.

Erik, als afstudeerder heb je een belangrijke bijdrage geleverd aan de inhoud van dit proefschrift. Daarnaast was de periode van onze prettige samenwerking voor mij een zeer leerzame. In dit verband wil ik ook de stagiaires Luuk en Bobby bedanken.

Marlies, jou ben ik zeer erkentelijk voor het ontwikkelen van de analyse applicaties, de prettige samenwerking daarin en het feit dat je altijd bereid was analyseproblemen á là minute op te lossen.

Ook wil ik een aantal medewerkers van het URLV bedanken voor hun bijdrage. Hans Turksma ben ik erkentelijk voor de volatile analyses en de zinvolle discussies. Wijnand Schuijl en Teun de Joode dank ik voor het uitvoeren van de LC-MS
The montmorillonite catalysed conversion of hydroperoxides

analyses. Matthias Berger, Johan Eshuis en Michael Gude dank ik voor hun betrokkenheid en hun commentaar.

Tenslotte wil ik alle AIO's, vaste medewerkers en studenten van de groep danken voor het creëren van de prettige werksfeer, waarin ik mijn onderzoek heb mogen verrichten. De onderlinge relatie was zo goed dat deze vaak verder ging dan de werkvloer. Hierbij denk ik aan LCT-uitstapjes, AOR-bezoeken, vloeistofententjes en squashpartijen, die bovendien zorgden voor de nodige ontspanning.
CURRICULUM VITAE

Stellingen
Behorende bij het proefschrift
THE MONTMORILLONITE CATALYSED CONVERSION OF HYDROPEROXIDES
van W.A. de Groot

1. De recente publicaties met lange lijsten van geïdentificeerde flavour componenten in ranzige oliën geven meer de vooruitgang in de ontwikkeling van analysemethodieken dan de vooruitgang in de begripsvorming van het ontstaan van deze componenten aan.

2. De wijze waarop door o.a. Hsieh en Kinsella en Frankel et al. het intermediair in het Hock mechanisme voor de ontleding van vetzuurhydroperoxiden door zuren wordt afgebeeld met de positieve lading op het zuurstofatoom is een zeer onwaarschijnlijke.
Hsieh R.J. en Kinsella, R.J. Advances in food and nutrition research 33 (1990), 233.

3. Veel reactiepaden van de ontleding van hydroperoxides gekatalyseerd door zuren, waarin het ontstaan van instabiele tussenprodukten een prominente plaats innemen, dienen te worden herzien.
Hoofdstukken 4 en 8, dit proefschrift.

4. De invloed van antioxidanten op oxiderende en geoxideerde lipiden is compleet verschillend bij kamertemperatuur en hogere temperaturen (> 100 °C), waardoor bij het afzetten van eigen resultaten tegen andere onderzoeken vaak appels en peren vergeleken worden.

5. De “Peroxide Value” (POV of PV) is een inadequate maat voor het voorspellen van de smaakstabiliteit van een oli.

6. Kleien zijn natuurlijke en goedkope sterk zure mineralen en zijn interessante katalysatoren voor vele reacties die gekatalyseerd worden door zuren.
Hoofdstuk 4 van dit proefschrift.
7. De recente veldslagen tussen rivaliserende sportverenigingen op ieder denkbaar niveau, maken dat “sport vervreemdt”, in plaats van dat “sport verbroedert”.

8. Gezien de recente reorganisaties waarbij werknemers met sommen geld op straat worden gezet kan een arbeidskracht ook goed worden beschouwd als een kapitaalgoed, dat in één keer kan worden afgeschreven.

9. De wens van de meeste oosteuropese landen voor aansluiting bij de NAVO, maakt het nut van het bestaan ervan op zijn minst discutabel.

10. De uitdroging van landbouwgronden in de zomer en de overstromingen in de winter van een paar jaar geleden, getuigen van een slechte waterhuishouding.

11. Het verplicht stellen van stellingen bij een proefschrift voor een promotie aan relatief jonge Nederlandse universiteiten, dit in tegenstroom aan het laten vervallen van deze stellingen aan een aantal oudere universiteiten, is een geforceerde manier om een zekere traditie te creëren.
13-\(c,t\)-HPOD
\[
\begin{align*}
\text{HOO} & \quad \text{13-hydroperoxy-9-cis,11-trans-octadecadienoic acid} \\
\text{R}_1 & \quad \text{R}_2 \\
\end{align*}
\]

13-\(t,t\)-HPOD
\[
\begin{align*}
\text{HOO} & \quad \text{13-hydroperoxy-9-trans,11-trans-octadecadienoic acid} \\
\text{R}_1 & \quad \text{R}_2 \\
\end{align*}
\]

9-\(c,t\)-HPOD
\[
\begin{align*}
\text{R}_1 & \quad \text{OOH} \quad \text{9-hydroperoxy-10-trans,12-cis-octadecadienoic acid} \\
\text{R}_2 & \\
\end{align*}
\]

9-\(t,t\)-HPOD
\[
\begin{align*}
\text{R}_1 & \quad \text{OOH} \quad \text{9-hydroperoxy-10-trans,12-trans-octadecadienoic acid} \\
\text{R}_2 & \\
\end{align*}
\]

9-c,\(t\)-HOD
\[
\begin{align*}
\text{R}_1 & \quad \text{OH} \quad \text{9-hydroxy-10-trans,12-cis-octadecadienoic acid} \\
\text{R}_2 & \\
\end{align*}
\]

9-\(t\),\(t\)-HOD
\[
\begin{align*}
\text{R}_1 & \quad \text{OH} \quad \text{9-hydroxy-10-trans,12-trans-octadecadienoic acid} \\
\text{R}_2 & \\
\end{align*}
\]

13-c,\(t\)-OTD
\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \quad \text{13-oxo-9-cis,11-trans-tridecadienoic acid} \\
\end{align*}
\]

13-\(t\),\(t\)-OTD
\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \quad \text{13-oxo-9-trans,11-trans-octadecadienoic acid} \\
\end{align*}
\]

ODE
\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \quad \text{12-oxo-10-trans-dodecenoic acid} \\
\end{align*}
\]

DD
\[
\begin{align*}
\text{R}_1 & \quad \text{CH}_3(\text{CH}_2)_3^- \\
\end{align*}
\]

\text{decadienal} \\
\text{(here: 2-trans,4-trans)}

\[R_1 \quad \text{CH}_3(\text{CH}_2)_3^- \quad \text{rest group 1}
\]

\[R_2 \quad -(\text{CH}_2)_6\text{C(O)OH} \quad \text{rest group 2}
\]
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Molecular Structure</th>
<th>Name</th>
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<tbody>
<tr>
<td>CHP</td>
<td><img src="image" alt="Cumene Hydroperoxide" /></td>
<td>Cumene Hydroperoxide</td>
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<tr>
<td>PH</td>
<td><img src="image" alt="Phenol" /></td>
<td>Phenol</td>
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<td>PP</td>
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<td>AMS</td>
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<tr>
<td>DCP</td>
<td><img src="image" alt="Dicumyl Peroxide" /></td>
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<tr>
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<tr>
<td>BCAK</td>
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<tr>
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<tr>
<td>DIM2</td>
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<td>DIM3</td>
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<td>CPE</td>
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<tr>
<td>CP</td>
<td><img src="image" alt="Cumyl Phenol" /></td>
<td>Cumyl Phenol</td>
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