

EuroBioRef

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	Name	Organization	Date	Visa
<i>Deliverable Responsible</i>	Bernhard RUSSBUELDT	CNRS-IRCELYON	28/01/2013	OK
<i>Work Package Leader</i>	Markus BRANDHORST	ARKEMA	28/01/2013	OK
<i>Sub-Project Leader</i>	Jean-Luc COUTURIER	ARKEMA	28/01/2013	OK
<i>Coordinator</i>	Franck DUMEIGNIL	CNRS-UCCS	02/02/2013	OK

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Executive summary

Description of the deliverable objective and content

The objective is the transformation of long chain unsaturated fatty molecules into shorter molecules suitable as aviation fuel additives. The goal of this task is to obtain nonanoic acid by oxidative cleavage of oleic acid or its derivatives using hydrogen peroxide. 500 g of nonanoic acid with a yield of 80% with respect to oleic acid was aimed for. Nonanoic acid may have an application in the form of an ester as fuel additive.

Brief description of the state of the art

The cleavage reaction of a saturated fatty acid using hydrogen peroxide passes by the formation of an epoxide and diol as intermediate. Other intermediates described as diketons, β -hydroxyperoxy alcohols, α -hydroxy ketones, were found during cleavage reactions.¹

Epoxidation of fatty acids is a well known reaction which is used industrially. The syn-dihydroxylation of olefins is most commonly performed in the presence of metal oxides, including KMnO_4 and OsO_4 , and $t\text{-C}_4\text{H}_9\text{OOH}$ with catalytic amounts of OsO_4 .² The anti-dihydroxylation can be achieved with $\text{CH}_3\text{CO}_3\text{H}$ and $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$ in water.³ Cleavage of oleic acid by different technologies is reviewed in detail in the article by A. Köckritz⁴ and by C. W. Jones⁵

Here a special focus is set on the literature on cleavage of fatty acids with hydrogen peroxide.

Daniel Swern published numerous articles about the reaction of hydrogen peroxide on fatty acids double bonds. The use of performic acid is reported to lead to ring opening and finally to dihydroxylation of the fatty acid even at low temperatures (-40°C).^{6,7} Findley et al. found that long reaction time and elevated temperatures favour the ring opening by acetic acids.⁸ In the presence of acid catalysts (H_2SO_4 ,⁹ BF_3 ¹⁰) even alcohols can open the epoxide forming an ether. Hölderich et al.¹¹ reported the addition of alcohols, like methanol, isobutanol and neopentanol to epoxidised oleates at 60°C in the presence of Amberlyst 15. Dihydroxylation of oleic acid by hydrogen peroxide and tungstic acid was studied by Luong et al.¹² It is postulated that the dihydroxy acid is the key interfacial agent in the oleic acid oxidation. Usui et al. obtained dihydroxylation of an oleic acid under metal free conditions using resin supported sulfonic acid (nafion SAC-13). Using a 4 fold excess of 30% hydrogen peroxide they report a 80 % yield of dihydroxy product after 20 h at 90°C .¹³

Dihydroxystearic acid or alcohol, obtained by the oxidation of oleic acid/alcohol with H_2O_2 , was cleaved under aerobic conditions using cobalt catalysts, also in combination with polyoxometallates or N-hydroxyphthalimide.^{14,15} In case of oleic alcohol cleavage, ω -hydroxynonanoic acid was obtained with a yield of $\sim 70\%$. Azelaic acid was only obtained with a yield of 52%.

¹ E. Antonelli, R. D'Aloisio, M. Gambaro, T. Fiorani, C. Venturello, J. Org. Chem., 1998, 63, 7190

² Y. Usui, K. Sato, M. Tanaka, Angew. Chem. Int. Ed., 2003, 42, 5623

³ Y. Usui, K. Sato, M. Tanaka, Angew. Chem. Int. Ed., 2003, 42, 5623

⁴ A. Köckritz, Eur. J. Lipid Sci. Technol., 2011, 113, 83-91

⁵ C. W. Jones RSC, Applications of hydrogen peroxide and derivatives p. 103

⁶ D. Swern, J. Scanlan, G. B. Dickel, Org. Synth, 1959, 39, 15;

⁷ D. Swern, G. N. Billen, T. W. Findley, J. T. Scanlan, J. Am. Chem. Soc., 1945, 67, 1786

⁸ T. W. Findley, D. Swern, J. T. Scanlan, J. Am. Chem. Soc., 1945, 67, 412

⁹ D. Swern, G. Billen, J. T. Scanlan, J. Am. Chem. Soc., 1948, 70, 1226

¹⁰ B. Hedman, P. Piispanen, E. Alami, T. Norin, J. Surfactants and detergents, 2003, 6, 47

¹¹ W. F. Hölderich, L. A. Rios, P. P. Weckes, H. Schuster, J. Synthetic Lubrication 20-4, 2004, 20, 289

¹² T. M. Luong, H. Schriftman, D. Swern, J. Am. Oil Chem. Soc., 1967, 44, 316

¹³ Y. Usui, K. Sato, M. Tanaka, Angew. Chem. Int. Ed., 2003, 42, 6523

¹⁴ E. Santacesaria, A. Sorrentino, F. Rainone, M. Di Serio, F. Speranza, Ind. Eng. Chem. Res., 2000, 39, 2766

¹⁵ E. Santacesaria, M. Ambrosio, A. Sorrentino, R. Tesser, M. Di Serio, Catal. Today, 2003, 79/80, 59

Novamont patented (WO93/12064) a method of oxidative cleavage of unsaturated fatty acids or esters by hydrogen peroxide using tungstic and molybdic acid or and alkaline salts thereof, in the presence of an onium salt as a phase-transfer agent. No solvent is used. Yield of methyl azelate of 77% were obtained. The onium salt as catalyst for oxidative cleavage was already claimed by Montedison in 1984 (EP0122804). Novance also describes a beneficial effect on the reaction rate of the presence of vicinal diol or epoxide of fatty acids at the beginning of the reaction of fatty acids and hydrogen peroxide using tungstic acid as catalyst (FR2789073).

Khlebnikova et al.¹⁶ described the cleavage of methyl oleate and methyl ricinoleate by hydrogen peroxide (30%) using an onium-type catalyst containing tungsten. A yield of ~84 % of azelaic acid was reported.

Solvay (US5321158) claimed a process for the production of dicarboxylic acids from unsaturated compounds or vicinal diols in organic solvent with Re(VII) and H₂O₂ as oxidising agent.

Few heterogeneous catalysts are reported for oxidative cleavage with hydrogen peroxide. For oleic acid, Cs₃PW₁₂O₄₀¹⁷ and WO₃ or Ta₂O₅ on Al₂O₃¹⁸ were investigated. Oxidative cleavage of cyclohexene with heterogeneous catalysts was carried out using Ti- and Ce-SBA-15¹⁹ and H₃PMo₁₂O₄₀ or H₃PW₁₂O₄₀ on Al₂O₃, ZnO or MgO as support²⁰.

Deviation from objectives and corrective actions

Heterogeneous catalyst showed significant lower activity than homogeneous catalysts. Therefore both types were investigated, since separation of the homogeneous catalyst was straightforward.

Innovation brought and technological progress

Published data often uses condition, which are not industrially applicable. A large excess of H₂O₂ is often used and almost never separation issues are addressed.

The work done in this task showed that cleaving unsaturated fatty nitriles has advantages over other raw materials like triglyceride, ester or even acid.

The amount of hydrogen peroxide was reduced as much as possible, solvent free conditions were used and separation issues were addressed, always keeping in mind an industrial scale up of the process.

Analysis of the results

The results are very encouraging since it proves the feasibility of oxidative cleavage with hydrogen peroxide of fatty molecules to two marketable products by a process that can be industrialised. However, the obtained yield is below the objective and needs to be further improved. In a simple two phase system nonanoic acid yield is 47% from oleonitrile and 33% from oleic acid. Addition of a phase transfer agent to oleic acid improved the yield to 66%. However, separation of products in a system using a phase transfer agent has to be looked at since the phase transfer agent probably has a negative impact on separation.

Conversion of oleonitrile/oleic acid was complete but the mass balance incomplete so that the main issue to be solved is the identification of unknown products. The potential for improvement of the yield is still high.

¹⁶ T. B. Klebnikova, Z. P. Pai, L. A. Fedoseeva, Y. V. Mattsat, React. Kinet. Catal. Lett., 2009, 98, 9

¹⁷ S. Turnwald, et al., J. Mater. Sci. Lett. 1998, 17,1305

¹⁸ H. Nouredini et al., J. Am. Oil Chem. Soc. 1999, 76, 305

¹⁹ M.N. Timofeeva, et al., Appl. Catal. A: Gen. 2008, 345, 195

²⁰ C.D. Brooks, et al., Chem. Comm., 1998, 37

Separation was addressed and ~100 g of pure nonanoic acid was obtained. This proves the possibility to obtain pure product from this process and 500 g, as requested in the DoW, could have been obtained, since enough cleavage product was obtained during the pilot run. The preparation of 500 g instead of only 100 g would not have brought any additional value to the task and distillation was thus not pursued.

The formation of a bifunctional molecule that can have a high value market is the driving force for this process. It increases the economical viability of the process. However, in the market addressed by the bifunctional molecules (polyester/polyamide) the product is a new player (9 carbons), which has to prove its technical performance and needs to go through validation procedures.

Impact of the results

The results show that oxidative cleavage is an interesting reaction for valorisation of fatty molecules. Nonanoic acid can be used as methyl ester in fuel application, although it is not a suitable jet fuel. The bifunctional cleavage product is suitable as monomer for polyamide or polyester. In both cases the market value is higher than in fuel applications and allows creating greater revenue from this process. The oxidative cleavage reaction of fatty molecules is feasible and remains a very interesting option in the transformation of oils in a bio-refinery. This confirms the choice of oxidative cleavage as a key element in value chain 2.

Related IPR

5 patents were filed by Arkema:

FR2970252

FR2970253

Filing number: FR11.56526

Filing number: FR11.61035

Filing number FR12.61611

Publishable information

Two patents are published. Since the deliverable is public, all information in this deliverable is publishable at the end of the project.

IRCELYON is planning to publish three articles on the following subjects

1. Oxidative cleavage of oleic acid using H_2O_2 in presence of tungstic acid in a biphasic system and the influence of the phase transfer
2. Preparation and characterisation of Ti, Zr, Nb and Ta incorporated MCM-41 using peroxy complexes
3. Performance of the early d block element oxides incorporated in different mesoporous silicas in the oxidative cleavage of oleic acid

Conclusion

The advantage of using fatty nitriles as raw material for oxidative cleavage with hydrogen peroxide under solvent free conditions was shown. **The obtained yield (47%) for nonanoic acid** in a two phase system **needs to be further improved to reach the deliverable target (80%)**. For oleic acid, the yield was much improved by addition of a phase transfer agent (33% → 66%).

Separation issues were addressed and **a 100g sample of pure nonanoic acid was obtained** from oleonitrile cleavage.

Among the heterogeneous catalysts the leaching needs still to be diminished and the activity improved. However, it could be demonstrated, that the peroxy complexes of the early d block metals are extremely valuable reagents for the incorporation of the corresponding oxides on different carriers. This confirms the pertinence of oxidative cleavage being a key element in value chain 2.

ANNEX I – Technical content

Arkema

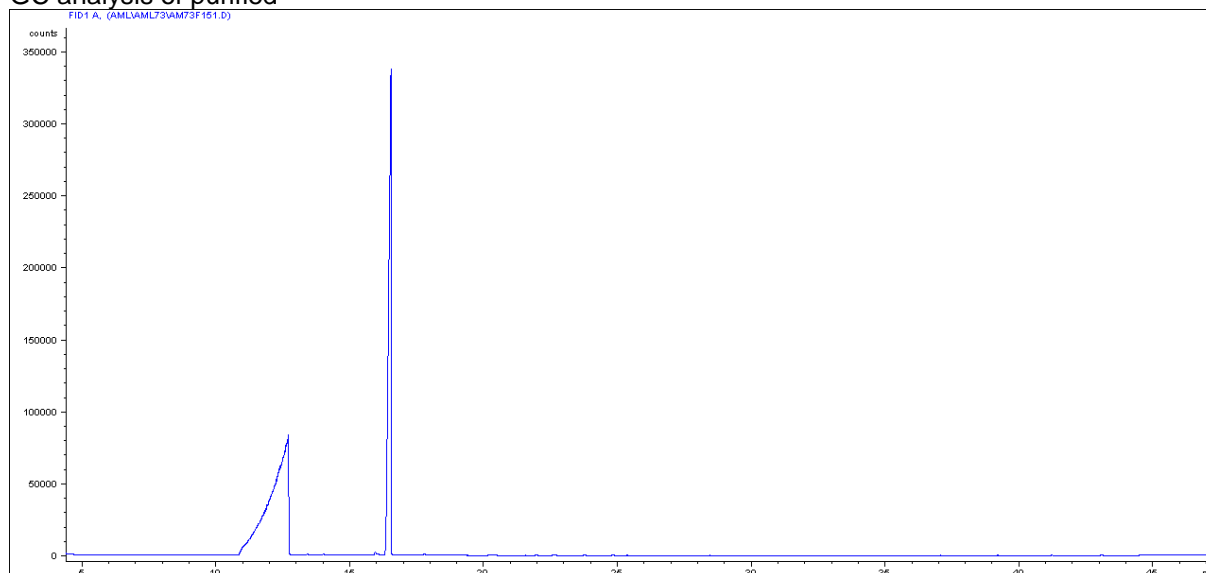
11.2 kg of nonanoic acid were obtained during a pilot run of oxidative cleavage of oleonitrile with a small stoichiometric excess of hydrogen peroxide using tungstic acid as catalyst under solvent free conditions. (See M30 report page 95 www.myndsphere.com/gm/document-1.9.370368/D11.1.5.3_30MInterimReport_CNRS_291012_VF.pdf)

The yield of nonanoic acid was 47%. Conversion of oleonitrile was complete. The mass balance of the reaction is incomplete and >30 % is not accounted for. A side reaction consuming nonanoic acid by the formation of dimeric or oligomeric molecules was identified

By separation and purification by distillation of a fraction of the cleavage product from the pilot run Arkema obtained a sample 81 g of pure nonanoic acid (96 %), which represents 70% of the engaged nonanoic acid.

By taking into account in addition other distillation fractions with high nonanoic acid content (but purity below 96%) 84% of nonanoic acid was recovered with a purity of 94%.

GC analysis of purified



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It was shown that it is possible to do the oxidative cleavage with neat oleic acid at an elevated reaction temperature of 80°C and more. Under these conditions the solidification of the product mixture can be avoided while the pelargonic acid and azelaic acid yields remain still high. A solvent is not required. A mass transfer restriction between the two liquid phases may be overcome by addition of emulsifiers and vigorous stirring.

For reference H_2WO_4 was used as homogeneous catalyst to prove the literature and the state of the art. In addition for a homogeneous system mass transfer problems are eliminated and it becomes easier to study the reaction mechanism. The optimization of the reaction temperature, H_2O_2 concentration and H_2O_2 addition duration was done. As optimum conditions the addition of 6 Equivalents 70% H_2O_2 in 6 h at 90°C and 48 h total reaction time was identified. As standard conditions 80°C was chosen, to prevent uncontrollable exothermic reaction. Using 1 mol% H_2WO_4 and 1 mol% Aliquat 336 phase transfer catalyst **65.8% pelargonic acid yield and 62.9% azelaic acid yield** are formed. The addition of the phase transfer agent has a considerable effect. Without phase transfer agent only 33.1% pelargonic acid yield and 35.4% azelaic acid yield can be achieved under otherwise same conditions. By total hydrolysis of the product scope it was shown, that especially esters between 9,10-dihydroxy stearic acid and the two product acids pelargonic acid and azelaic acid are causing the intermediates and an improved yield can be obtained after hydrolysis. The investigation of other phase transfer agents and/or emulsifiers is of great interest. Probably even longer reaction times are required.

In a first approach titanium silicalite TS-1 or post-synthetically titanated zeolites Y, BEA and MOR were tested. The poor results were attributed to diffusion problems and further tests with exclusive microporous catalysts were abandoned.

In addition nanosized ZSM-5 (approx. 100 nm) or high crystalline ZSM-5 (approx. 5 μm) was prepared in collaboration with a trainee student from Brazil. Different post-synthetic treatments were conducted by steaming and acid washing or desilication by etching with sodium hydroxide solution.

These are preliminary tests for the preparation of TS-1 nanoparticles or high crystalline TS-1 post-synthetically modified by desilication, which is leading to a bimodal micro- and mesopore system. TS-1 with a high external surface is expected to be a much more efficient catalyst for the oxidative cleavage reaction.

Heteropoly acids immobilised as cesium salt e.g. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ either as bulk catalyst or supported on SBA-15 were investigated, too. A large partition of leaching of the heteropolyacid and uncontrollable homogeneous catalysis was noted.

Furthermore Nb_2O_5 , Ta_2O_5 , MoO_3 and WO_3 supported on ZrO_2 , Y_2O_3 stabilised ZrO_2 or La_2O_3 stabilised ZrO_2 were made by a novel method. A high dispersal of the mentioned metal oxides was obtained by anion-exchange of the corresponding metal peroxo complexes on the different $\text{Zr}(\text{OH})_4$ carriers. The catalytic testing was abandoned due to vigorous H_2O_2 decomposition.

TiO_2 , ZrO_2 , Nb_2O_5 and Ta_2O_5 incorporated in the silica network of MCM-41 were prepared. Scale-up was successfully done and the catalysts were obtained in batches of 3 moles SiO_2 . Again the corresponding metal peroxo complexes could be successfully used for the incorporation of the aforementioned metals. The metal dispersal by TEM and XPS mapping needs to be confirmed.

Using 10 wt% Ta-MCM-41 containing 12.8 wt% Ta_2O_5 and standard conditions, 8.7% pelargonic acid yield and 8.1% azelaic acid yield are obtained.

TiO_2 and Ta_2O_5 incorporated in SBA-15, TiO_2 , ZrO_2 , Nb_2O_5 , Ta_2O_5 , MoO_3 and WO_3 incorporated in SBA-16 and TiO_2 and Ta_2O_5 incorporated in KIT-6 could be successfully made with high structural order, too. The catalytic testing of these materials needs to be completed.