Oxidative Cleavage of Oleic Acid to Produce Added Value Products

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INTRODUCTION

MIRINZ has an interest in processing by-products from meat processing to produce added value chemicals and biochemicals. One such procedure is the oxidative cleavage of oleic acid (obtained from beef and mutton tallow) to azelaic and pelargonic acids:

$$\underset{\text{Oleic acid}}{CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH} \xrightarrow{\text{Oxidative Cleavage}} \underset{\text{Azelaic acid}}{HOOC(CH_2)_7COOH} + \underset{\text{Pelargonic acid}}{CH_3(CH_2)_7COOH}$$

The major industrial production of azelaic acid is via ozonolysis of oleic acid. Ozone is environmentally friendly, leaving no residues at the end of the reaction. However, ozonolysis is expensive, due to the highly technical equipment used, and large a electricity consumption.

Sodium hypochlorite (NaOCl) has also been used for the oxidative cleavage of oleic acid. Although it is cheaper than ozone, NaOCl can be corrosive in the presence of some catalysts, such as ruthenium tetroxide. Chlorinated by-products may be formed in the reaction, and a strongly alkaline mixture of NaCl and NaOH is left at the end of the reaction.

This paper reports trials using hydrogen peroxide as the oxidant, to cleave oleic acid using various transition metal catalysts (Tsen *et al.*, 1995; Turnwald, 1997). This reaction has several benefits; for example the by-product is water, and a high proportion of the H_2O_2 (47% by weight) is available as active oxygen.

TRIALS USING PCWP CATALYST

Materials and Methods

The first transition metal complex tested as a potential catalyst for the oxidation reaction was peroxo-tris(cetylpyridinium)12-tungstophosphate (PCWP). The complex was prepared by reacting cetylpyridinium chloride (CPC), a phase transfer catalyst, with 12-tungstophosphoric acid (WPA) in a H_2O_2 environment.
Ishii *et al.*(1988) described the oxidation of 1,2-diols, ketones, and olefins using H_2O_2 with heteropolyacid phase transfer catalysts. The method developed for oleic acid oxidation using the PCWP catalyst was modified from Ishii *et al.*'s method for olefin oxidation.

"Priolene" was used as the oleic acid source (Priolene is 50% oleic acid). This was heated to reflux with 50% H_2O_2 and the catalyst. Priolene is a liquid at room temperature, so no solvent was necessary. The effect of varying reaction times, amounts of catalyst and volumes of H_2O_2 was investigated, as was the method of H_2O_2 addition - either in one portion at the beginning of the reaction, or in stages during the reaction.

Results and Discussion

Reactions using the PCWP complex were successful in producing azelaic and pelargonic acids (Tsen *et al.*, 1995). After the oxidation was completed, the aqueous (H_2O_2/water) and organic fractions were separated and azelaic acid, a solid at room temperature, precipitated out of both fractions. Pelargonic acid, a liquid at room temperature, was present in the organic fraction. Any remaining catalyst was precipitated from the organic fraction with ethanol.

In a 2 hr reaction using 1 g catalyst and 35 mL H_2O_2, 75% azelaic acid and 66% pelargonic acid were recovered from 10 g oleic acid. In a 2 hr reaction using only 0.18 g PCWP catalyst, product yields were low, suggesting that the reaction had not gone to completion.

Reaction times were increased to 5 or 10 hours, in an attempt to improve the reaction performance at low catalyst concentration. Increasing the reaction time from 2 to 5 hours doubled the yield of azelaic acid (16% to 32%), but increasing the reaction time further, to 10 hours, led to only a small increase in azelaic acid yield (32% to 37%).

H_2O_2 loss through decomposition, either thermally or by the PCWP catalyst, was determined by titration at the end of reactions where Priolene was replaced by water. For the 5 hr reaction, H_2O_2 loss through decomposition was 47%, and for the 10 hr reaction, it was 42%.

An excess of H_2O_2 is required for the oxidation reaction to proceed successfully. Stoichiometrically, 0.16 moles of the oxidant is needed, without accounting for decomposition by heat or catalyst, which is up to 0.27 moles in a 5 hr reaction. In addition, oxidation of other unsaturated fatty acids present in Priolene would consume H_2O_2, as PCWP is not a specific catalyst.

Considering both the stoichiometric amount of H_2O_2 required and the known quantity lost through thermal or catalytic decomposition, the minimum oxidant needed for a successful reaction is 0.405 moles, or 24.1 mL. In this investigation, 35 mL H_2O_2 was used.

Higher yields of the product acids were obtained when the H_2O_2 was added in three portions during the reaction. Addition of the oxidant in two stages - 10 mL at the beginning of the reaction, and 25 mL 2.5 hours into a 5 hr reaction, was not as effective. With this latter method, most of the oxidant was added to the reaction mixture with only half the reaction time remaining. This late addition of the H_2O_2 to the reaction system meant that it did not have time to oxidise the oleic acid effectively.

Electrospray Mass Spectrometry
The spectrum of the PCWP catalyst gave peaks that were assigned to the cetylpyridinium ion. No peaks due to the tungstophosphate portion of the catalyst were observed. Spectra of azelaic acid isolated at the completion of the reaction gave no indication of the cetylpyridinium ion, showing peaks due to azelaic acid only. Pelargonic acid and the cetylpyridinium ion were present in the organic fraction.

Conclusions
When a small quantity of PCWP catalyst (0.18 g) was used, a 5 hr reaction time gave the best performance for oxidation of oleic acid. Increasing the reaction time beyond 5 hours did not result in a proportional increase in product yields.

A small amount of PCWP was recovered from the organic fraction of the 5 hr reaction. At the completion of the 10 hr reaction, no catalyst could be recovered, indicating that the PCWP had decomposed in this time. Although a small quantity could be recovered with the 5 hr reaction, the catalyst was to a large extent unrecoverable, as it presumably breaks down into the cetylpyridinium ion and tungstophosphate fragments during the oxidation.

A large excess of H_2O_2 was needed for the oxidation of oleic acid, because a significant amount of the oxidising power of the hydrogen peroxide was spent by catalytic and thermal decomposition. Priolene liquid also contains several other fatty acids and the oxidation of these acids also had to be taken into account when determining the amount of oxidant required.

TRIALS USING $MOO(O_2)[C_5H_3N(CO_2)_2](H_2O)$ CATALYST

For these studies (Turnwald, 1997), the reaction was scaled down from that investigating PCWP. The PCWP complex was used as a control catalyst, to ensure that oxidative cleavage occurred on the reduced scale that was used.

Various seven-coordinate molybdenum peroxo complexes that are stabilised by chelate picolinato or pyridine-2,6-dicarboxylato ligands have been reported as both stoichiometric (Jacobsen *et al.*, 1979) and catalytic (Thiel and Priermeir, 1995) reagents for the epoxidation of olefins, allylic and homoallylic alcohols, and the Baeyer Villiger oxidation of cyclic ketones (Jacobsen *et al.*, 1978). In this study a metal peroxo complex, oxoperoxo(pyridine-2,6-dicarboxylato)molybdenum(VI)hydrate, $MoO(O_2)[C_5H_3N(CO_2)_2]H_2O$, was tested. This complex is easily formed by the reaction of suitable molybdenum oxo compounds with pyridine-2,6-dicarboxylic acid in the presence of H_2O_2.

Results and Discussion
The electrospray mass spectrum of the aqueous fraction from the oxidation using $MoO(O_2)[C_5H_3N(CO_2)_2](H_2O)$ showed large peaks due to azelaic acid. Quantitative GC analysis of the oxidation reaction products showed that the molybdenum complex was more effective for the oxidative cleavage of oleic acid than the PCWP complex. Although both complexes gave a complete turnover of oleic acid, PCWP gave 8.8 wt % azelaic acid, and 6.9 wt % pelargonic acid, whereas $MoO(O_2)[C_5H_3N(CO_2)_2](H_2O)$ gave 15.9 wt % azelaic acid, and 12.7 wt % pelargonic acid. All reaction products were analysed as fatty acid methyl esters (FAMES).

Mechanism of $MoO(O_2)[C_5H_3N(CO_2)_2](H_2O)$ Catalysed Oxidative Cleavage
It is difficult to propose a mechanism of action for a catalytic process without performing kinetic studies, and fully investigating all products at the end of the reaction. However, several investigations on Mo peroxo complexes have been carried out, and it is possible that the mechanism of oleic acid oxidation with $MoO(O_2)[C_5H_3N(CO_2)_2](H_2O)$ and H_2O_2 resembles those proposed for other olefin oxidations. If so, oxidation of oleic acid by H_2O_2 and $MoO(O_2)[C_5H_3N(CO_2)_2](H_2O)$ may proceed by epoxidation of the acid, followed by ring opening of the epoxide to give a diol. The reaction system in this investigation contains H_2O_2/water, as well as various carboxylic acids present in the organic substrate. These acids may make the reaction system acidic enough for the formation of a 1,2- diol from the epoxide.

Venturello and Ricci (1986) has proposed a mechanism for the oxidative cleavage of 1,2-diols with H_2O_2 and a heteropolyacid catalyst. It is possible that a similar mechanism is involved in the $MoO(O_2)[C_5H_3N(CO_2)_2](H_2O)/H_2O_2$ catalytic system. The first step would involve the peroxo moiety of the catalyst being protonated to give a hydroperoxy group. This may be followed by the formation of an adduct between the diol and the Mo catalyst, then the formation of an α-hydroxy ketone. This ketone may then undergo nucleophilic attack by H_2O_2. Fragmentation of this adduct would result in the cleavage products, i.e. an acid and an aldehyde. The aldehyde would be further oxidised to a carboxylic acid.

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