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Double bond oxidative cleavage of monoenic fatty chains

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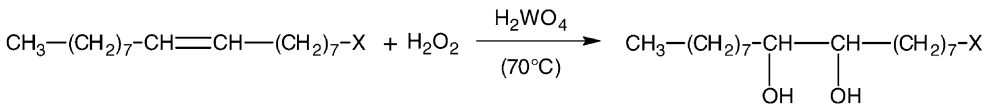
Abstract

A two steps process for the production of azelaic acid and pelargonic acid or alternatively of ω-hydroxynonanoic and pelargonic acid, starting from respectively oleic acid and oleyl alcohol has been studied. In the first step, the monoenic reagent reacts with hydrogen peroxide, in the presence of pertungstic acid, as catalyst, to give the corresponding diol (hydroxylation of the double bond). In the second step, the reaction mixture obtained in the first step containing the formed diol and the exhausted catalyst, was additioned of cobalt acetate and reacted with molecular oxygen (oxidative cleavage of vicinal diols). As the first step has largely been studied in the literature, the study of the nature of the catalytic site and of the catalytic mechanism of the second step of the process is the main subject of this work with the objective of identifying, for this step, an independent and reusable catalyst. In particular, we focused our attention on the diol deriving from oleyl alcohol, because reagents and products are more easily separated and analyzed. The study of the mentioned reactions is complicated by the presence of respectively two or three phases in the reactor. The "in-situ" formed catalyst, active in the second reaction step, seems to be a lacunary poly-oxometalate in which cobalt, sequestered by the tungstate anion groups and accessible to the reagent, is the active component. This has been shown by polarographic analyses of the catalyst solution before and after the reaction, and is also confirmed by the observation that cobalt, sequestered by EDTA, in the absence of tungstic acid is active, too.

Keywords: Double bond oxidative cleavage; Fatty chains; Azelaic acid

1. Introduction

In this paper, the catalytic aspects involved in a new process for the production of azelaic and pelargonic acids and of ω-hydroxynonanoic and pelargonic acid by oxidative cleavage of the double bond of, respectively, oleic acid and oleyl alcohol, in two reaction steps will be studied. In the first step, the monoenic reagent reacts with hydrogen peroxide in the presence of pertungstic acid catalyst, giving diol as the reaction product, as in the following reaction scheme:



where X could be –COOH or –OH.

The second step corresponds to the oxidative cleavage, with molecular oxygen, of the diol formed in the first step, in the presence of an "in-situ" formed catalyst obtained by reaction between the exhaust pertungstic acid, used in the first step, and cobalt acetate

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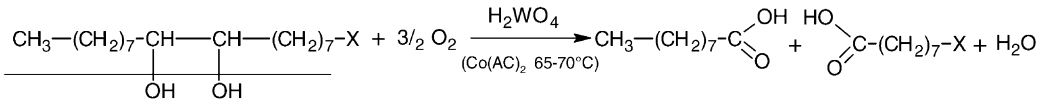
added before initiating the second step. The second step occurs with the following stoichiometry:



The first reaction, in the absence of solvents, occurs in a liquid–liquid phase system and has been studied by different authors [1–4]. In a previous work the authors have optimized the experimental conditions for this reaction [1]. The conversion is never complete (86% for oleic acid and 98% for oleyl alcohol), because, the reaction system becomes a doughy mixture that cannot be efficiently stirred, in particular, when oleic acid is the reagent. However, positive effect on both conversion and yields can be achieved with the use of a particular solvent (2-propanol), giving place to a unique liquid phase, or by introducing a small amount of preformed diol [1]. The observation of the formation of small amounts of epoxide suggests a rection mechanism in which epoxide is formed as intermediate.

Very few information can be found, on the contrary, related to the second step of the reaction, that is, the oxidative cleavage of the obtained diol. In this step of the process, described only in [1,5], a solution of cobalt acetate is simply added to the first step reaction mixture and the reaction is performed by adding oxygen, under moderate pressure, in an autoclave. The reaction occurs, in this case, in a gas–liquid–liquid three-phase system, showing a brief induction time, probably due to the "in-situ" catalyst formation, as shown in [1]. The present work is mainly devoted to the achievement of more information about this second reaction step, regarding the active specie and the reaction mechanism with the aim to find a catalyst independent from the first stage of reaction that can more easily be recycled. The discovery that by mixing the exhaust catalyst of the first step, a metastable form of tungstic acid, with a cobalt salt [6], giving place to an active and selective catalyst in the oxidative cleavage of vicinal diol, is certainly a very interesting insight in the perspective of realizing a new industrial process. However, by operating in this way, the recycle of the catalyst is complicated. The disposal of two different catalysts, each independently recycled, therefore, is imperative for the process feasibility. In order to do this, we need to know the nature of the catalytic specie formed by mixing metastable tungstic acid and cobalt acetate. At this purpose, it is known from the literature that tungstic acid is insoluble in water, while, on the contrary, pertungstic acid is completely soluble [6]. It is also known, that tungstic acid obtained by reduction or decomposition of mononuclear pertungstic acid, favored by the presence of cobalt, precipitates very slowly, occurring some days for observing a precipitate [6]. It appears, reasonable, therefore, that cobalt ions can react with tungstate anions giving different more or less ordered species and, in a limit situation, cobalt ion could act as templating agent for obtaining polyoxometalates with a well defined structure, such as, the Keggin, the Dawson or the Anderson structures [7]. In these structures, normally, cobalt ion is not accessible, because, completely surrounded by tungstate groups. Starting from the observation that tungstic acid, coming from the first step of reaction, is not active without the addition of cobalt acetate and cobalt acetate alone is not active, too, the mixture of the two components gives place to a new catalytic specie that must be individuated and if possible reproduced. We have made some different attempts to artificially reproduce the active catalytic specie. In particular, we prepared and tested some polyoxometalates (POM), such as, for example $H_6CoW_{12}O_{40}$ (Keggin's structure) and $(NH_4)_8[Co_2W_{12}O_{42}]$. As it will be seen, the activities resulted generally low and some experimental observations indicate that observed activities are not due to the original well structured POM but to successively formed lacunary POMs in which cobalt atoms are directly accessible to the reagent. That is, tungstate anions have merely the scope of activating cobalt as a consequence of sequestration. This suggested the idea of testing, as catalyst, a solution of cobalt in the presence of sodium salt of EDTA (ethylendiaminotetracetic acid), in the absence of tungstic acid. This catalyst resulted active and selective in the reaction. This clearly open the perspective of using two independent and reusable catalysts, one for each step, that is a useful

condition for the development of the industrial process.

2. Experimental section

2.1. Apparatus, methods and reagents

Hydroxylation runs have mainly been performed by using oleyl alcohol, as reagent, because, the separation and analysis of the reaction products, in both the reaction steps, are easier than starting from oleic acid. This gives us the opportunity of a more accurate investigation. However, we observed in the past that the results achieved by using oleyl alcohol as reagent can also be extended to oleyc acid. Hydroxylation reaction has been performed in a 500 cm^3 glass-jacketed reactor thermostatted, at 70 °C, with a recirculating liquid. As the reaction is strongly exothermic, a cooling metallic coil of stainless steel, fed with cold water, was put inside the reactor for a better control of the temperature. About 80 g of oleyl alcohol (furnished by Aldrich with a purity of 85%) were, normally, loaded in the reactor together with 0.60 g of powdered tungstic acid (H_2WO_4, Aldrich, 98%), then 24 g of concentrated hydrogen peroxide (60% by weight, provided by Ausimont SpA) stabilized with small amounts of sodium stannate and sodium pyrophosphate, were added dropwise by using a dripping funnel mounted on the reactor. The high hydrogen peroxide concentration is necessary, because, we observed that a threshold concentration of 30% by weight was necessary to start the reaction. The hydrogen peroxide stabilization is necessary to overcome its decomposition, strongly favored in the presence of the mentioned catalyst. Initially, three phases are present in the reactor: the oil liquid phase, containing the organic reagent, the aqueous phase, containing the hydrogen peroxide and a solid phase of tungstic acid. The first drops of hydrogen peroxide added, completely dissolve tungstic acid, by forming pertungstic acid, and the reaction mixture, initially yellow, decolorates and the phases in the reactor become two immiscible liquids. The temperature of 70 °C is necessary not only for obtaining a reasonable reaction rate but also for having the oil in a fluid form. The reaction is prosecuted for about 2 h. The reaction product, 9,10-di-hydroxystearyl alcohol, can be separated from the reaction mixture by dissolving it in ethyl acetate and purified by recrystallization. Pure 9,10-di-hydroxystearyl alcohol, separated by the reaction mixture can be used for performing the second step of reaction, in a controlled way, by introducing a catalyst of a well defined composition, such as, for example, a polyoxometalate (POM) or a complex of cobalt with EDTA. Alternatively, the reaction mixture, coming from the first reaction step, is put directly in an autoclave, added with a solution of cobalt acetate (1.2 g of $Co(CH_3COO)_2{\cdot}4H_2O$, from Aldrich, in 300 cm^3 of water) and used for the second step of reaction, that is, the oxidative cleavage of the formed diol (use of the reference catalyst). When the reaction mixture coming from the first step is directly loaded in the autoclave, the addition of cobalt acetate determines the fast decomposition of any residual amount of hydrogen peroxide, being cobalt salts very active in decomposing hydrogen peroxide.

The cleavage reaction is performed, as mentioned, in an autoclave equipped with a motor driven blade stirrer rotating at 500 rpm, for 3 h, at about 65–70 °C, under 45–50 bars of air pressure. These conditions are kept constant for all the time of the run. Therefore, pure oxygen was added during the run, for compensating the oxygen consumed as a consequence of the reaction, taking constant the pressure in the autoclave. The reaction, normally, shows an induction time of about 20 min. The reaction, performed by using the reference catalyst, has been followed by withdrawing small samples of the reaction mixture, at different reaction times, and analyzing by gas chromatography both the acqueous and organic phase of the withdrawn samples. Gas chromatographic analyses have been made after derivatization of the samples treated with N,O-bis(tri-methyl-sylil) acetamide dissolved in pyridine [1]. All the performed runs are reported in Table 1, with the related experimental adopted conditions. As mentioned, some runs have been made also in the presence of two polyoxometalates that are respectively $H_6CoW_{12}O_{40}$ and $(NH_4)_8[Co_2W_{12}O_{42}]$. These compounds have been prepared, in our laboratory, by following the methods suggested by the literature [8,9]. Polarographic analyses have been made on the aqueous phase before and after the reaction for many different runs. Analyses have been performed by using a polarograph Metrohm 646VA, with a differential method, using pulses of 50 mV. However, more experimental details are reported elsewhere [1].

Table 1
Conversion, selectivity and products distribution for different catalysts O: ω-hydroxynonanoic acid, P: pelargonic acid, A: azelaic acid

Run	Catalyst	Conversion (%)	Selectivity (%)[a]	O (wt.%)	P (wt.%)	A (wt.%)
1	Traditional catalyst: 1.2 g $Co(CH_3COO)_2 4H_2O$: 300 ml distilled water	99	74.9	36.6	33.7	3.9
2	Co:W 1:12: 0.047 g $Co(CH_3COO)_2 4H_2O$: 300 ml distilled water: 1.1 g CH_3COONa	34.8	5.7	1.2	0.6	0.2
3	Na_2WO_4 and Co acetate: 0.73 g $Na_2WO_4 2H_2O$: 1.25 g $Co(CH_3COO)_2 4H_2O$: acetic acid to pH 3	19.3	42.5	4.1	4.1	0.0
4	$(CoW_{12}O_{40})^{6-}$: W concentration $= 7.5 \times 10^{-3}$ M	25.3	32.0	4.6	3.5	0.0
5	$(NH_4)_8[Co_2W_{12}O_{42}]$ pH 7.0: 0.63 g $(NH_4)_8[Co_2W_{12}O_{42}]$: 300 ml distilled water: 1.17 g CH_3COONa	10.7	0	0.0	0.0	0.0
6	$(NH_4)_8[Co_2W_{12}O_{42}]$ pH 3.9: 0.63 g $(NH_4)_8[Co_2W_{12}O_{42}]$: 300 ml distilled water: acetic acid to pH 3.9	25.4	53.5	5.9	7.7	0.0
7	$(NH_4)_8[Co_2W_{12}O_{42}]$ pH 2.0: 0.63 g $(NH_4)_8[Co_2W_{12}O_{42}]$: 300 ml distilled water: H_2SO_4 (98%) to pH 2.0	34.4	53.8	8.7	9.8	0.0
8	Co–EDTA complex: 2.12 g $NaCo(EDTA)4H_2O$: 300 ml distilled water	45.8	92.4	16.3	26.0	0.0

Product distribution has been made in wt.% because some by products and related molecular weight were unknown. Run conditions: oxygen partial pressure 15 bar; total pressure 45 bar; temperature 70 °C; autoclave volume 500 cm^3.

[a] Selectivity to useful products = (O + P + A) per conversion.

3. Results and discussion

The kinetic behavior of the second step reaction in the presence of the catalyst obtained by adding cobalt acetate to the reaction mixture, coming from the first step, (reference catalyst) can be seen in Fig. 1. From data reported in Fig. 1, it appears that some azelaic acid is also obtained for long reaction times. We have attempted, first of all, to artificially reproduce the reference catalyst simply by mixing in a solution sodium tungstate (run 3 of Table 1). Cobalt tungstate, insoluble of pink colour, was initially formed. By adding acetic acid, in such amount to obtain pH 3, the tungstate was completely dissolved. In the autoclave, pure 9,10-di-hydroxystearyl alcohol was, then, added to the acqueous solution containing this catalyst for undertaking the reaction by keeping about the same ratio between reactant and catalyst of the reference run (run 1 of Table 1). The activity and product distribution obtained, in this case, can be compared with the ones obtained by using the reference catalyst. By comparing data reported in Table 1, it is possible to conclude that the catalyst prepared from sodium tungstate and cobalt acetate shows a low activity, this means that the active specie has been obtained but only at low concentration level. A way to recognize the formation of the active specie is to examine the tungstate solution before and after the reaction, by polarography. As it can be seen, in Fig. 2, the two obtained polarograms are quite different and this means that tungstate anion has changed its redox properties during the reaction. It is also interesting to observe that the polarogram obtained after the reaction, has some common features with the polarogram related to the reference catalyst, that is reported in Fig. 3. It is possible to distinguish in this polarogram a peak at −0.4 V falling about in the same zone or before the peak corresponding to the molecular oxygen reduction. As, the solutions have been accurately outgassed by flowing nitrogen for a long time, this peak corresponds to a highly oxidant specie. We always observed this peak for any cobalt-tungsten based catalyst showing activity, therefore, it is reasonable to suppose that this peak identify the active specie. However, very probably, this specie is in equilibrium with others less active or not active ones considering the presence of other peaks corresponding to different redox properties. In order to identify the active specie we have, then, prepared and tested, as a catalysts for the reaction, two different polyoxometalates, that are: a Co-tungstate anion with

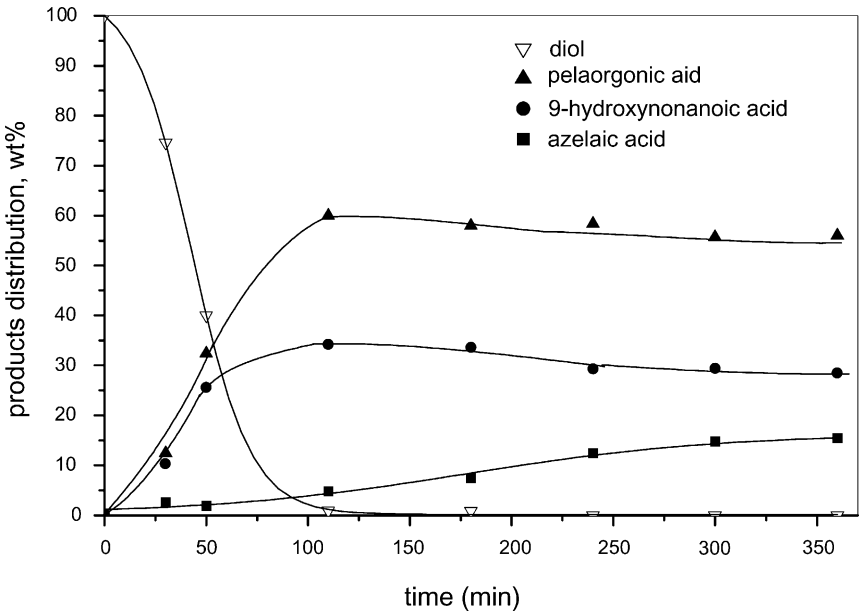


Fig. 1. Evolution with time of the composition of the organic phase in the run of oxidative cleavage of 9,10-hydroxystearylic alcohol (run conditions: oxygen partial pressure 15 bar; total pressure 45 bar; temperature 70 °C; autoclave volume 500 cm^3; reference catalyst).

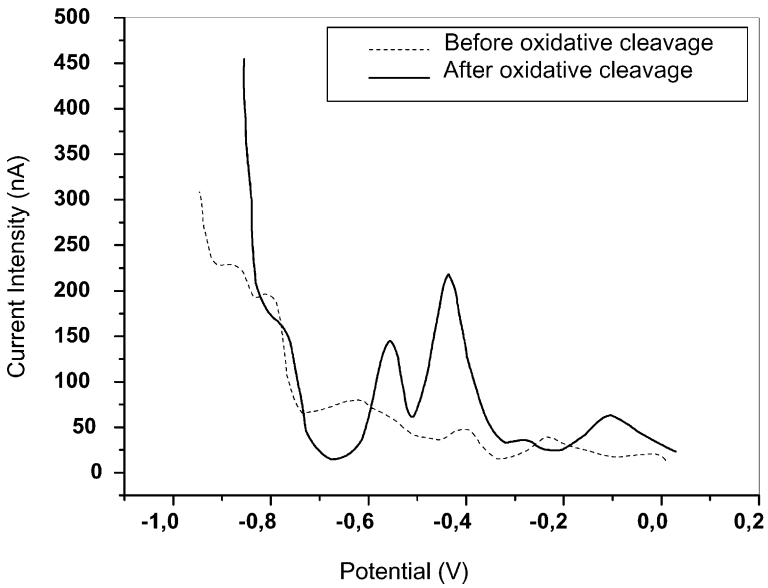


Fig. 2. Comparison between polarographic traces before and after the reaction of oxidative cleavage with reference to the run with $(NH_4)_8[Co_2W_{12}O_{42}]$ at pH 2 (run conditions: oxygen partial pressure 15 bar; total pressure 45 bar; temperature 70 °C; autoclave volume 500 cm^3).

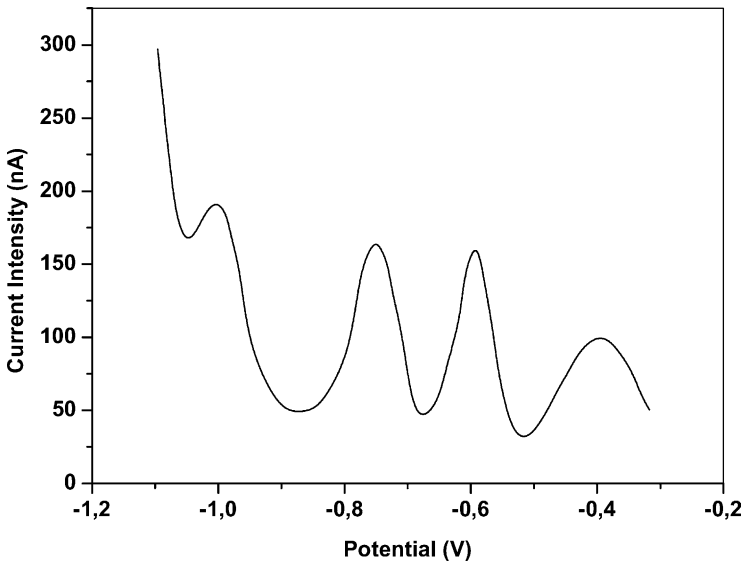
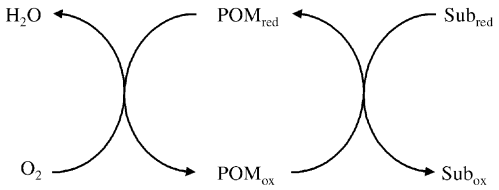


Fig. 3. Polarographic analysis of the aqueous phase after the oxidative cleavage of 9,10-hydroxystearilic alcohol. Run performed with reference catalyst (run conditions: oxygen partial pressure 15 bar; total pressure 45 bar; temperature 70 °C; autoclave volume 500 cm^3).

the Keggin structure $(CoW_{12}O_{40})^{6-}$ and a binuclear complex of the type $(NH_4)_8[Co_2W_{12}O_{42}]$. This last has been tested in three different pH conditions that are: neutral, acid at pH 3.9 and at pH 2. The correction of pH at 3.9 has been made by adding CH_3COOH, the correction at 2, with H_2SO_4. The activities obtained for all the mentioned runs have been reported always in Table 1 and can be compared with the one obtained by the reference catalyst. By comparing these data it is possible to conclude that polyoxometalate performs better than the simple mixture of sodium tungstate and cobalt acetate but are still much less active than the reference catalyst. Activity is not due, therefore, to the polyoxometalates itself but to products obtained from their decomposition. This can also be deduced by observing that the solution of polyoxometalate, before the reaction, does not shows, at the polarographic analysis, any trace of the peak at −0.4 V, characteristic of the active specie, as it can be seen in Fig. 2. To become active polyoxometalate has to lost the original structure. The $(NH_4)_8[Co_2W_{12}O_{42}]$ POM, that has not given activity in neutral conditions, shows a moderate activity at pH 3.9 and a higher activity at pH 2. However, even if, this last activity is always lower than the one obtained by the reference catalyst, this behavior is very important because it is known from the literature [8] that this POM is very stable at neutral pH, while, at low pH this POM release Co^{2+} ions. This suggests the formation of lacunar POMs in which cobalt ions, sequestered by tungstate groups, are accessible to the reagents and this should be the active site. The polarograms of the solution, after the reaction, at different pH, show again the appearance of the peak at −0.4 V for the lower pH, that means that POM has lost the original structure. On the basis of these observations we can conclude that, very probably, in the active catalyst, tungstate anions groups have merely the function of sequestering cobalt ions, greatly changing the redox potential of the ionic couple Co^{2+}/Co^{3+}. If this hypothesis is correct other sequestering agents could be used for activating cobalt. We have, therefore, used Co sequestered with EDTA as catalyst. The obtained results are always reported in Table 1 and, as it can be seen, are very encouraging for both activity and selectivity. The conclusion is that cobalt promote the reaction but only when is opportunely sequestered and the redox potential of the couple Co^{2+}/Co^{3+} must be high enough to sustain the redox cycle. It is not clear, whether or not the mechanism of the reaction is homolytic or heterolytic. Runs performed in the presence of a radical initiator, such as AIBN, the anti-oxidant 2,6 di-tert-butylphenol or a

radical scavenger substance, such as 2-propanol, have not had influence on the reaction rate and on the induction time, as it has been shown in a previous work [1]. This seem to exclude the homolytic mechanism. On the other hand an heterolytic mechanism requires the involvement of a very powerful catalytic redox specie promoting a catalytic cycle similar to the one suggested by Weinstock [10] for polyoxametalates, that is:



In which POM should be substituted, in this case, by Co-sequestered complex. That is, it cannot be excluded that oxygen is directly activated by cobalt after coordination giving an highly reactive peroxy group.

4. Conclusions

In this paper the oxidative cleavage of the C–C double bond of the unsaturated fatty chains, occurring in two steps reaction (hydroxylation and oxidative cleavage of vicinal diol) has been studied. In particular we have focused our attention to the second reaction step that is less known and less studied in the literature. We started our study by using a catalyst that is formed in situ simply by mixing the reaction mixture coming from the first step with cobalt acetate, because, this catalyst has shown satisfactory performances. We have demonstrated, with the aid of polarographic investigation, that catalyst formed in this way is a lacunary POM with Cobalt ions accessible by the reagent. The role of tungsten anion is simply that of sequestering cobalt increasing the Redox Potential of the couple Co^{2+}/Co^{3+}. This has been confirmed by the observation that by using EDTA, as sequestering agent, in the absence of tungstate anion good activities and selectivities were obtained. On the other hand, the industrial feasibility of the process is clearly conditioned by the availability of independent and reusable catalysts for each step of reaction. The use of EDTA or other more efficient sequestering agents open, therefore, the perspective to realize a new industrial process.

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