Double Bond Oxidation of Unsaturated Fatty Acids

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Different oxidizing agents for performing the cleavage oxidation of the double bond of the unsaturated fatty acids are presented, and their economic performance is analyzed. Ozone and sodium hypochlorite are the most commercially efficient oxidants.

Laboratory work for the oxidation of oleic acid to azelaic and pelargonic acids using hypochlorite as oxidant is described. The advantages of working in an emulsion system and using $RuCl_3$ as a catalyst are discussed, and a possible mechanism of the reaction is presented. A flow sheet for an industrial process based on this concept is proposed. A simulation of a plant using this technology is made by a computerized model, and the economic parameters obtained permit us to conclude that the sodium hypochlorite can be an interesting reagent for industrial oxidations of double bonds in fatty acids.

Some processes in the oleochemical industry include the oxidation of the double bond of unsaturated fatty acids. A representative example of such a reaction is the oxidation of the oleic acid in order to obtain pelargonic and azelaic acids:

$$\underset{\text{oleic acid}}{CH_3(CH_2)_7CH = CH(CH_2)_7\,COOH} \longrightarrow 2O_2$$

$$\underset{\text{pelargonic acid}}{CH_3(CH_2)_7\,COOH} + \underset{\text{azelaic acid}}{HOOC(CH_2)_7\,COOH} \qquad \text{(a)}$$

The oxidative cleavage of the double bond of the unsaturated fatty acids is usually performed in a liquid phase by a number of oxidizing agents. Prior to any laboratory work we have compared, from a techno-economic point of view, those oxidation agents which are presented in Table 1. In order to facilitate such a comparison, the concept of "chemical function" as presented by U. Colombo has been used (1). In our case the chemical function of the oxygen donors is the oxidation of a double bond with its cleavage into two carboxylic groups:

$$-HC = CH- + 2O_2 \longrightarrow 2x(-COOH) \qquad \text{(b)}$$

The efficiency of an oxidizing agent (OE) is defined as the cost of the oxidant (OC) necessary to perform the reaction (b).

$$OE = 2.10^{-3}\,(OC)[MW(Ox)](Ox.St)^{-1} \qquad \text{(c)}$$

OE = efficiency of oxidant ($/ton double bond cleaved and oxidized)
OC = cost of oxidant ($/ton oxidant)
MW(Ox) = molecular weight of oxidant.
Ox.St = stoichiometric ratio oxidant/active oxygen (as in reaction b)

The OE values for the relevant oxidants are presented in Table 2. We are aware that those figures do not give the complete image of the oxidation process and that supplementary parameters such as oxidation potential, yield of the process, physical conditions of the reaction, safety and ecological considerations can change the order of the oxidants' efficiency presented in Table 2. Yet the use of the algorithm (c) can furnish a first tool for choosing oxidants for industrial operations.In the above specific situation the best economic efficiencies are presented by ozone and sodium hypochlorite.

Use of ozone. The production of ozone and the oxidation process of oleic acid are described in a recent article (2). The use of ozone as oxidant presents some advantages, namely high reactivity, selectivity and lack of residues or by-products. In our opinion, those benefits are overwhelmed by shortcomings including:

- Need for special high technology equipment for the production of ozone, which implies a large capital

TABLE 1

Commercial Oxidants

Oxidant	Reaction	Generated oxygen mol O_2/mol oxid.
Potassium permanganate	$K_2Mn_2O_8 + H_2O \rightarrow 2MnO_2 + 2KOH + 3/2O_2$	1.5
Potassium bichromate	$K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3/2O_2$	1.5
Chromic acid	$2CrO_3 \rightarrow Cr_2O_3 + 3/2O_2$	1.5
Hydrogen peroxide	$H_2O_2 \rightarrow H_2O + 1/2O_2$	0.5
Ozone	$O_3 \rightarrow 3/2O_2$	1.5
Sodium hypochlorite	$NaOCl \rightarrow NaCl + 1/2O_2$	0.5

TABLE 2

Cost Efficiency of Various Oxidants

Oxidant	Price of oxidant $/ton[a]	Active oxygen generated ton oxygen/ ton oxidant	Cost of active oxygen $/ton active oxygen	Cost of double bond oxidation $/tmol
Potassium permanganate	2400	0.152	11,500[b]	740[b]
Potassium bichromate	1056	0.163	6480[c]	415[c]
Chromic acid	2596	0.480	5410	345
Hydrogen peroxide	710	0.235	3020	195
Ozone	1505[d]	0.666	2260	145
Sodium hypochlorite	425[e]	0.216	1967	126

[a]Prices quoted are f.o.b. USA, May 1986.
[b]A value of $605/ton potassium permanganate has been allocated for the by-product MnO_2.
[c]The value of by-product potassium sulfate is considered equivalent to the cost of sulfuric acid.
[d]The cost of ozone has been calculated as in reference (3) with cost of electricity at $0.05/kilowatt hr.
[e]The price of sodium hypochlorite considers a total conversion for chlorine and 95% conversion for sodium hydroxide. A value of $45/ton has been allocated for operating costs.

investment ($17,000/kg ozone/hr installed capacity) and great annuity costs.

- Dilution of the ozone in the feed (1.5-2% ozone in weight), which implies an increase in the volume of gases to be processed with a negative influence on the kinetics of the oxidation reaction.
- High dependence on energy costs, due to a great consumption of electricity.

As a consequence of this situation, to the best of our knowledge, only one company uses ozone for the production of azeleic and pelargonic acids.

Use of sodium hypochlorite. From the list of oxidants presented in Table 2, sodium hypochlorite is the least expensive. Its preparation is relatively simple, with a yield of 95-100%, and concentrated solutions can be obtained. No sophisticated equipment is necessary for its preparation and use; therefore, the investment is minimal. The residues from the sodium hypochlorite preparation and use are solutions of sodium chloride. Therefore, we have tested its potential as an oxidant for unsaturated fatty acids.

In order to perform the oxidation reaction, one must assure a satisfactory mass transfer between the oil phase and the aqueous solution of sodium hypochlorite. One possible way of performing this task is to use a phase transfer catalysis (PTC) technique. A report on the use of sodium hypochlorite as a cooxidant (with ruthenium tetroxide) of alkenes in a PTC operation has been published (4). The actual commercial price of quaternary salts used as PTC catalysts ($10-14,000/ton) is limiting the industrial use of the PTCs to the production of fine or specialty type chemicals which can reach values of at least $7,000-10,000/ton. (5) This price level is out of range for the products of the oleochemical industry.

An alternative way to assure a satisfactory mass transfer between the oil phase and the sodium hypochlorite solution is the use of surface active agents. Stable o/w emulsions can be formed with droplets 0.2-1 microns in size and have very large surface areas (6). The addition of sodium hypochlorite as an oxidizing agent to such emulsions permits oxidation of the double bond at the interface of the oil droplets. Such reactions have potential selectivity and good chances to cleave double bonds.

Experimental procedures. A stable emulsion consisting of 0.2-1 μm droplet size has been prepared using:

10% (w/w) oleic acid
1% (w/w) Brij 35, ethoxylated lauryl alcohol
89% (w/w) Water

The emulsion was prepared by mixing all the ingredients at once at 25 C by stirring (magnetic) for 10 min. One hundred g (0.035 mol) of the above emulsion was added to a sodium hypochlorite solution (0.035 mol). The reaction mixture was maintained at 20 C and pH = 12.5, with mechanical stirring for 50 min, after which another 0.177 mol of sodium hypochlorite solution and 1.7×10^{-4} mol $RuCl_3$ was added, and the

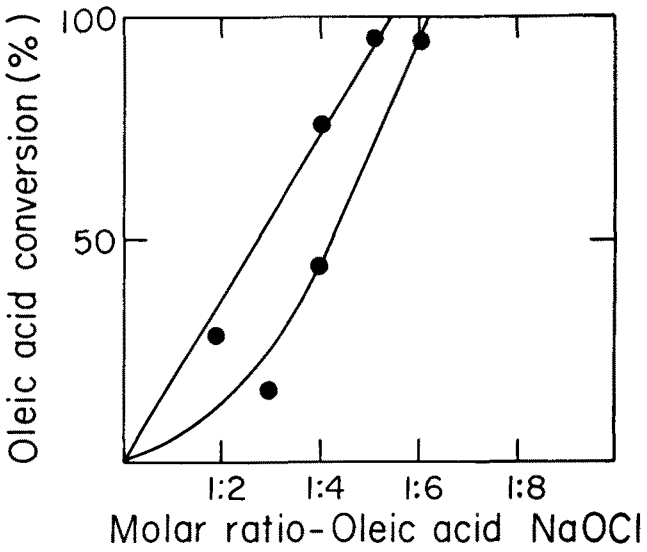

FIG. 1. Conversion as function of oxidant quantity—catalyzed reaction; a, in emulsion; b, nonemulsified. Reaction mixture composition (w/w): Oleic acid, 10%; Brij 35, 1%; water, 89%; catalyzator 1/100 molar relative to oleic acid. Temperature, 10 C; time, 8 hr.

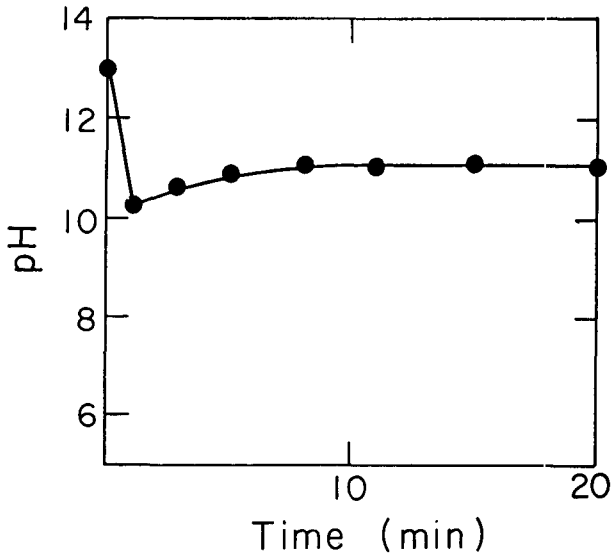

FIG. 2. Change of pH with time—reaction in emulsion. Reaction mixture composition (w/w): oleic acid, 10%; emulsifier Brij 35, 1%; water, 89%; 117-ml solution of sodium hypochlorite 8.3M/10 gr of oleic acid.

reaction was continued for one more hr. At the end of the reaction the solution has been acidified with hydrochloric acid (15%, w/w). The organic phase was extracted with hot water and the azelaic acid was separated in the aqueous solution. The remaining organic phase consists of pelargonic (70%), dihydroxy stearic, stearic, palmitic and myristic acids. The pelargonic acid may be separated by distillation from this mixture. The azelaic acid has been separated, with a yield of 80%, from the aqueous solution by crystallization and filtration. The initial water phase which contains the catalyst has been treated with isopropanol in order to recover the $RuCl_3$. A degree of recovery of 75% has been attained in the laboratory. The analyses were carried out by GC using standard procedures.

RESULTS AND DISCUSSION

In order to check the relevance of the emulsification operation, the oxidation stages also have been performed on a nonemulsified mixture of oleic acid, solution of hypochlorite and catalyst. It has been found that when the reaction is performed in an emulsion system, some important advantages occur in comparison with the nonemulsified (heterogenous) system. For a given molecular ratio hypochlorite/oleic acid, it has been found that in emulsion systems a higher conversion of oleic acid is attained. The results are presented in Figure 1. The use of the emulsion system has also permitted a reduction of the reaction time needed to obtain the desired oleic conversion (85%) from 10 to 2 hr.

From the exploratory experiments, the following conclusions have been reached:

- In this specific system the ruthenium chloride accelerates the decomposition of the hypochlorite. Therefore, part of the hypochlorite present in the system can be decomposed before acting as an oxidant agent.
- Prior to the cleavage of the double bond, an oxidative process forming a dihydroxy fatty acid takes place.
- The intermediary oxidative process conducting to the dihydroxy acid can be done without catalyst.

Therefore, we propose that oxidation of oleic acid by hypochlorite should be carried out in three consecutive stages:

- Emulsification of oleic acid in water, using Brij 35 (ethoxylated lauryl alcohol) as surface active agent. Brij 35 has been selected because its hydrophobic chain is stable to oxidation.

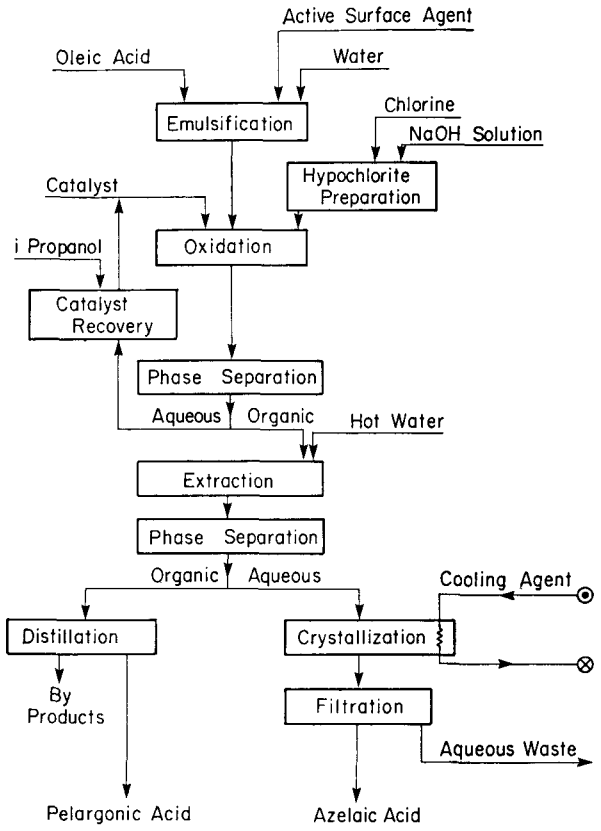

FIG. 3. Oxidation of oleic acid with Na hypochlorite. Possible flowsheet of industrial operation.

TABLE 3

Basic Assumption of the Techno-economic Simulation

Yield of oxidation:	90% relative to oleic acid 65% relative to sodium hypochlorite
Cost of raw materials:	as in *Chemical Marketing Reporter*, May 1986.
Indirect labor:	40% of direct labor
Maintenance:	3% of fixed capital investment
Packaging:	$30 per ton
Sales expenses:	10% of total sales value
Depreciation:	Straight line method; 10 years
General and administrative expenses:	3.5% of total sales value
Factory administration:	40% of direct labor
R & D expenses:	4% of total sales
Working capital:	for an average of 30 days

- Noncatalytic oxidation. In this stage the double bond of the oleic acid has to be oxidized to give 9-10 dihydroxy stearic acid.

$$CH_3(CH_2)_7\,CH{=}CH(CH_2)_7\,COOH \xrightarrow[NaOH]{NaOCl} CH_3(CH_2)_7\,\underset{OH}{CH}\,-\,\underset{OH}{CH}\,-\,(CH_2)_7\,COOH$$

In this step one mole of sodium hypochlorite and sodium hydroxide are consumed, as it appears from Figure 2, in which a sharp drop in the pH is observed.

- Catalytic oxidation. In this stage the 9-10 bond of the 9,10 dihydroxy stearic acid previously formed is oxidatively cleaved. Pelargonic and azelaic acids are formed.

$$CH_3(CH_2)_7\,\underset{OH}{CH}\,-\,\underset{OH}{CH}\,-\,(CH_2)_7\,-\,COOH \xrightarrow[RuCl_3]{NaOCl} CH_3(CH_2)_7\,COOH + HOOC\,-\,(CH_2)_7\,-\,COOH$$

$RuCl_3$ is used as a co-oxidant and is recovered at the end of the reaction.

An industrial procedure for the oxidation of oleic acid will comprise a two-stage reaction between the acid contained in the water/oil emulsion droplets and the hypochlorite present in the aqueous phase, followed by the separation of phases. The $RuCl_3$ used as catalyst will be recovered from the aqueous phase. The azelaic acid will be extracted from the organic phase with hot water and separated in a further sequence by crystallization. The pelargonic acid is obtained by the distillation of the remaining organic phase (Fig. 3).

TABLE 4

Profit and Loss Account—Mature Year[a]

	000$/yr	$/ton	% Gross sales
Gross sales	43,600.0	2,180.0	100.0
Direct mfg cost (1-7)	32,688.1	1,634.4	75.0
1. Raw materials	31,999.4	1,600.0	73.4
2. Direct labor	129.0	6.5	0.3
3. Indirect labor	51.6	2.6	0.1
4. Maintenance	266.3	13.3	0.6
5. Supplies	39.9	2.0	0.1
6. Utilities	1.8	0.1	0.0
7. Packaging	200.0	10.0	0.5
8. Marketing expense	872.0	43.6	2.0
Overheads (9-13)	3,078.8	153.9	6.5
9. Depreciation (str line)	887.7	44.4	2.0
10. General & admin.	1,526.0	76.3	3.5
11. Factory admin.	51.6	2.6	0.0
12. Local taxes & insurance	177.5	8.9	0.0
13. Research & development	436.0	21.8	1.0
Total product cost (1-13)	36,639.0	1,831.9	83.5
Gross profit	6,961.0	348.1	16.5
Net profit after 40.0% tax	4,176.6	208.8	9.9

Breakdown of costs:

Component	% Product cost
Raw materials (1)	87.3
Capital related (4 + 5 + 9)	3.3
Labor related (2 + 3 + 11)	0.6
Sales related (7 + 8)	2.9
Energy related (6)	0.0
Overheads (10 + 12 + 13)	5.8

Variable costs (1 + 6 + 7 + 8) = 1,653.7 $/ton (90.3% of cost)
Fixed costs (2 + 3 + 4 + 5 + 9 + 10 + 11 + 12 + 13) = 178.3 $/ton (9.7% of cost)

[a]Production, 20,000.0 tons/yr.
Production: 10,800 T/yr azelaic acid; 9,200 T/yr pelargonic acid.
Sales prices $/ton: azelaic acid 2,700; pelargonic acid, 1,540.

TABLE 5

Economic Performance

Yearly cash flow

Production year	% Plant utilization	Cash flow (000$)
0	0.0	-5,917.95
1	80.0	-6,212.53
2	85.0	+5,382.02
3	90.0	+5,908.36
4	100.0	+6,961.04
5	100.0	+6,961.04
6	100.0	+6,961.04
7	100.0	+6,961.04
8	100.0	+6,961.04
9	90.0	+5,908.36
10	80.0	+19,353.93

Economic parameters

Maximum cash exposure ($000)	21,040.8
Profit	4176.6 $000/yr (9.89% of sales)
Payback time	2.1 yr
Break-even price	1827.1 $/ton
Break-even production	6774.6 tons/yr (33.9% of capacity)
Return on investment	47.1%
Net present value ($000):	
For rate of return of 10.0%	27,114.3
For rate of return of 15.0%	18,440.6
Internal rate of return	+42.2%

Economic evaluation. An economic analysis of a possible industrial venture based on the above proposed technology has been done. A computerized model of a chemical plant, batch operated, established at the Casali Institute (7) has been used to simulate the production of 20,000 tons/y of acids (9,000 T pelargonic; 11,000 T azelaic). The technical and economic assumptions on which this simulation is based are summarized in Table 3.

The economic image predicted for the plant for a typical mature year is presented in Table 4, and the economic parameters to be realized appear in Table 5. It seems that the economic performance of the proposed process is good as demonstrated by the indicators, Return on Investment (47%) and Internal Rate of Return (42.2%). The process has a high degree of stability to eventual changes in the economic environment, as shown by the low break even values.

The laboratory experiments and the techno-economic analysis prove that sodium hypochlorite is a suitable oxidation agent able to replace ozone in this specific application.

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