Permanganate Oxidation of Oleic Acid Using Emulsion Technology

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ABSTRACT

Free oleic acid is emulsified in water and oxidized using potassium permanganate, to azelaic and pelargonic acids together with dihydroxy-, ketohydroxy- and diketo-stearic acids at neutral pH. The yield and the products distribution are controlled by: the type of emulsifier and its concentration; the oleic acid concentration in the emulsion; and the oleic acid-oxidant ratio.

The most common and feasible method of preparing azelaic acid in good yields involves the oxidative cleavage of natural unsaturated fatty acid containing the $-CH=CH(CH_2)_7CO_2H$ grouping (1,2).

Mild oxidizing agents such as performic acid, acetic acid, alkaline hydrogen peroxide, osmium tetraoxide or potassium permanganate will oxidize oleic acid in aqueous solution only to dihydroxy, ketohydroxy and diketo acids (3-5). Many attempts have been made to improve the permanganate oxidation of unsaturated compounds, including the use of crown ethers (6) and phase-transfer catalysts (7-9). It is notable that the oxidation of methyl oleate to methyl azelate and methyl pelargonate has been achieved using a combination of phase-transfer catalyst and RuO_2 (10).

Surfactants and macromolecules are increasingly used as reaction media in which the rates of the reaction products, distribution and stereochemistry are affected (11), and therefore, in the course of our studies on emulsion technology, we looked for possible organic reactions to be done in oil-in-water emulsions.

To the best of our knowledge, the only two oxidations that have been carried out in emulsion are the emulsion ozonization of cyclolefins in aqueous alkaline hydrogen peroxide (12) and the autoxidation of linoleic acid in micellar system (13).

We wish to report the oxidation of free oleic acid in neutral oil in water emulsion causing the formation of dihydroxy, ketohydroxy, diketo acids and the cleavage of the double bond yielding azelaic and pelargonic acids.

Technical-grade oleic acid, analar potassium permanganate and commercially available (Atlas Europol) nonionic emulsifiers were used. Three main groups of emulsifiers were used: polyoxyethylene ethers of long-chain fatty alcohols ("Brijs"), polyoxyethylene esters of long-chain fatty acids ("Myrjs"), long-chain carboxylic acid esters of polyoxyethylenated sorbitol, sorbitan and isosorbides ("Tweens").

Prior to any oxidation reaction, an emulsion between the fatty acid and water was formed (N. Garti and E. Avni, submitted for publication) and charged into a 5-necked flask equipped with mechanical stirrer, built-in pH meter, condenser, a CO_2 inlet to control the pH during the reaction and thermocouple attached to a temperature controller. The reaction flask was cooled to 10 C. A pulverized potassium permanganate was added at once. Samples were withdrawn in constant intervals, quenched with SO_2 (to reduce the MnO_2 formed during the oxidation), and analyzed by gas liquid chromatography (GLC) and other standard methods (10).

No oxidation was observed in a control reaction when

TABLE I
Products Distribution Obtained from Oleic Acid Oxidation with Permanganate Carried Out in Oil-in-Water Emulsion Using Brij 35 (HLB 16.9) As Emulsifier[a]

					Yield of products (mol %)		
Preparation method[b]	Oleic acid (wt %)	$KMnO_4$/ oleic[c]	Emulsifier (wt %)	Conversion (mol %)[d]	Azeleic	Diol-, ketol-, diketo-stearic respectively	Unidentified products
I	5.7	2	0.5	71	11	23, 17, 11	9
III				75	20	14, 20, 13	8
II				79	37	12, 18, 10	2
II	5.7	2	0.5	79	37	12, 18, 10	2
	8.5			70	31	(29)	10
	14.2			59	28	(33)	8
II	5.7	2	0	2	0	(2)	0
			0.1	15	3	(12)	0
			0.2	50	11	(30)	9
			0.5	79	37	(40)	1
			1.0	85	56	(26)	3
			2.0	80	42	(31)	7
			3.0	56	45	(10)	1
II	5.7	1	0.5	37	6	(21)	10
		2		79	37	12, 18, 10	2
		3		79	56	(15)	8
		4		98	84	(9)	5
		6		98	87	(8)	3

[a] Reaction conditions: 10 C, mechanical stirring at 1,200 rpm, ½ hr.

[b] I) oleic acid, water and emulsifier mixed together. II) oleic acid was added dropwise to aqueous emulsifier solution. III) aqueous emulsifier solution was added dropwise to the oleic acid.

[c] Molar ratio

[d] Calculation based on 100% oleic acid

TABLE II

Effect of the Nature of the Emulsifier and Required HLB on the Oleic Acid Oxidation in Emulsion Oxidation by Permanganate[a]

Emulsifier	HLB	Chemical composition	Oleic acid conversion (mol %)
Brij 35	16.9	Polyoxyelhylene-lauryl ether	78.7
Myrj 52	16.9	Polyomyelhylene stearate	72.5
Tween 20	16.7	Polyoxyelthlene sorbitan lauryl ester	66.2
Myrj 49	15.0	Polyoxyethylene stearate	60.0
Myrj 51	16.0	↓	71.8
Myrj 52	16.9		72.5
Myrj 53	17.9		78.0
Myrj 59	18.8		80.1

[a] $KMnO_4$/oleic = 2; 5.7% oleic in water; 0.5 wt % emulsifier; 10 C; 30 min; 1,200 rpm.

permanganate was added to a two-phase mixture of oleic acid and water in the absence of the emulsifier, even after vigorous stirring.

Table I summarizes some of the results obtained in the oxidation reaction done at various proportions of oleic acid, permanganate and emulsifiers.

It is clear that the conversion of oleic acid is affected by the method of preparation of the emulsion and that the best results are obtained when the emulsion is prepared by adding the oil into the aqueous solution containing the emulsifier. Emulsification of the fatty acid with increasing amounts of emulsifier improves the oxidation up to an optimal concentration. Best conversions to azeleic acid are obtained when an excess of oxidant is used. Increasing the oil concentration causes a decrease in the yields of the reaction and a significant decrease in the azelaic acid formation.

Table II illustrates the effect of the nature of the emulsifier and the best hydrophilic-liphofilic balance (HLB) required from the emulsifier to be used for the emulsion formation.

The nature of the reaction, mechanistic aspects and the effect of the emulsion stability on the yields, rates and product distribution will be discussed in a separate report (N. Garti and E Avni, submitted for publication).

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[Received December 29, 1980]