Catalytic Autoxidation of 9(10)-Formylstearic Acid

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ABSTRACT

A procedure has been developed for the preparation of carboxystearic acid by catalytic autoxidation of hydroformylated oleic acid. This autoxidation is catalyzed effectively with Ca, Cu, Co, Fe, Mn and Ce naphthenates in either acetone or glacial acetic acid at 20 C. With the exception of Ca, all these catalysts produce from 2 to 10% keto- and hydroxystearic acids as byproducts. Yields of up to 95% 9(10)-carboxystearic acid are obtained by autoxidation for 24 hr with Ca naphthenate (0.5% Ca based on formylstearate). This autoxidation period was shortened to 7 hr by using a binary catalyst (0.5% Ca and 0.05% Mn), which affords a minimum of side products.

INTRODUCTION

The procedure for catalytic oxidation of hydroformylated oleate (1) has been modified for the oxidation of 9(10)-formylstearic acid. Without a solvent, carboxystearic acid crystallized as a white solid on flask walls, and adequate mixing could not be achieved.

EXPERIMENTAL PROCEDURES

Materials and Analyses

The preparation of molecularly distilled 9(10)-formylstearic acid was described previously (2); its purity exceeded 93% by gas liquid chromatography (GLC). Impurities included oleic and stearic (3-4%), carboxystearic (2-3%) and an unidentified material (0-1%). Neutral equivalent: 300; calculated, 312. Methylation, GLC techniques and analytical procedures have been described (1). Methyl stearate was the internal standard, and calculated yields were based on area.

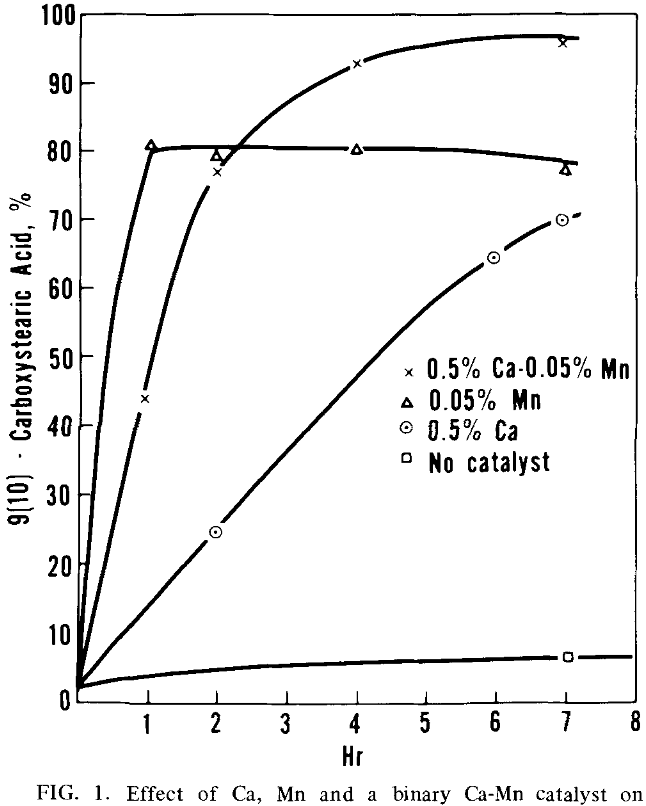

FIG. 1. Effect of Ca, Mn and a binary Ca-Mn catalyst on formation of carboxystearic acid at 20 C.

Catalytic Autoxidations

Either acetone or glacial acetic acid was used to maintain solution during autoxidation. Distilled 9(10)-formylstearic acid (25 g) and the metal naphthenate catalyst (0.05-0.55% metal based on weight of acid) were charged into a 250 ml three-necked round-bottomed flask, and 100 ml solvent was added. Compressed air (dried with Drierite) was passed at the rate of 18-20 liters/min through an ebullator into the reaction solution stirred magnetically for 24 hr. Samples were analyzed periodically by GLC. On a large scale the procedure was similar, except that a 5 liter flask and 750 ml acetone with 750 g 9(10)-formylstearic acid (92%) and 74 ml catalyst solution (5% Ca) were used. The yield was 877 g crude 9(10)-carboxystearic acid (86% by GLC, 79% by acid value).

Purification

Crude 9(10)-carboxystearic acid was purified either by distillation or urea crystallization after treatment with dilute sulfuric acid to remove catalyst. The following procedure was used: Crude 9(10)-carboxystearic acid (194 g) was dissolved in 1 liter diethyl ether and transferred to a separatory funnel where it was shaken with 200 ml portions of 0.5 N sulfuric acid until precipitation was complete. After water washing and solvent removal, the product (186 g) was catalyst-free. Yield of calcium sulfate: 2.6 g.

Catalyst-free 9(10)-carboxystearic acid (181 g, 86%) was distilled in an alembic flask at 0.01 mm Hg. Two main fractions (total weight: 146 g; bp 203 C) were collected (neutral equivalents, 164.7 and 159.5; theory 164). Yield of 9(10)-carboxystearic acid was 80.7%.

To remove straight chain impurities, a urea crystallization procedure was adopted (1). From 370 g crude autoxidized product was obtained 292 g 9(10)-carboxystearic acid (95%). Neutral equivalent: 171; calculated, 164.

RESULTS AND DISCUSSION

Data in Table I are limited to those experiments when autoxidations are near completion. The highest yield (95%) of 9(10)-carboxystearic acid was obtained with a binary catalyst of 0.5% Ca and 0.05% Mn as naphthenates. By using the combination of Ca-Mn, we were able to accelerate the rate of autoxidation to approach that of Mn alone, with a minimum formation of keto and hydroxy byproducts.

Figure 1 shows rates of formation of 9(10)-carboxystearic acid from autoxidations of 9(10)-formylstearic acid catalyzed with 0.05% Mn, 0.5% Ca and a binary combination of 0.05% Mn-0.5% Ca. The yield of carboxystearic acid was higher with the binary Ca-Mn catalyst than with either Mn or Ca naphthenate catalysts. Although the autoxidation with 0.05% Mn was essentially over in 1 hr, more than 10% was byproduct. Autoxidation with 0.5% Ca required 24 hr for completion, and keto- and hydroxystearic acids formed in only trace amounts. After a 24 hr reaction without any catalyst, ca. 89% formylstearic acid remained compared to 3.5% in the autoxidation with Ca. Autoxidation with the Mn-Ca catalyst was complete in 7 hr, and only 0.8% keto- and hydroxystearic acids were produced.

Although Ca is the least active autoxidation catalyst, it is

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TABLE I

Catalytic Autoxidation of 9(10)-Formylstearic Acid[a]

Catalyst[b]	Time, hr	Product composition, GLC, %					Acid value, % carboxystearic
		Carboxystearic	Formylstearic	Stearic + oleic	Keto- + hydroxystearic	Other[c]	
Control	24	7.2	89.2	3.6	Nil	Nil	—
0.5% Ca	7	69.8	26.7	3.5	Nil	Nil	—
	24	94.4	3.5	2.1	Trace	Trace	87.0
0.5% Cu	24	82.8	3.8	3.8	2.5	7.1	69.5
0.5% Co	4	79.3	0.5	4.9	8.8	6.5	68.3
0.5% Fe	4	82.8	7.9	5.2	2.2	1.9	71.2
0.05% Mn	1	81.7	1.3	2.8	10.4	4.4	—
0.5% Ce	7	80.6	4.9	5.4	8.2	0.9	—
0.5% Ca 0.05% Mn	7	95.3	0.8	2.5	0.8	0.6	84.0
0.5% Ca 0.05% Ce	6	78.5	14.1	3.1	2.7	1.6	74.0

[a] Starting material: 93.5% formylstearic, 2.3% carboxystearic, 3.3% stearic + oleic, 0.9% unidentified.

[b] Per cent metal (as naphthenates) based on 9(10)-formylstearic acid.

[c] Includes: epoxystearic, dicarboxystearic, other unidentified material.

the most efficient for the conversion of formyl- to carboxystearic acid. Autoxidations with Co, Mn, Ce, Cu and Fe naphthenates are characterized by side reactions. The order of activity for byproduct formation in our work approximates Co>Mn>Ce>Cu>Fe. Side reactions from these autoxidations can be attributed to free radical catalysis (3-5).

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