Catalytic Hydroformylation of Unsaturated Fatty Derivatives with Cobalt Carbonyl

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ABSTRACT

Two cobalt-carbonyl oxo processes were developed to prepare useful products in high yield from fatty derivatives. In one process, hydroformylation in the presence of MeOH at 120 C gives dimethyl acetal esters from either methyl oleate or oleic acid. In the other, a two-step process, hydroformylation (120 C) followed by hydrogenation (180 C) gives better yields of hydroxymethyl esters from both mono- and polyunsaturated fatty substrates. Recycling the cobalt catalyst was demonstrated for the second process. The acetal and acetoxymethyl derivatives of the oxo products have utility as polyvinyl chloride plasticizers.

INTRODUCTION

Hydroformylation of unsaturated fatty derivatives has been reviewed (1). Properties of C_{19} hydroformylation products vary according to the catalyst system used, and many areas of applications for these oxo products are known.

With methyl oleate, conventional hydroformylation catalyzed by cobalt carbonyl produces a complex mixture of isomeric formyl and hydroxymethyl derivatives (2-4). In marked contrast, selective hydroformylation catalyzed by rhodium-triphenylphosphine produces a mixture almost exclusively composed of 9 and 10 isomers of methyl formylstearate (5). The expensive rhodium catalyst, recoverable from the solid support and distillation residues, remains active and can be recycled (6). On this basis, a laboratory-batch process for hydroformylating methyl oleate was developed that permitted recycling of the rhodium catalyst without significant loss of activity (7).

With polyunsaturated substrates, hydroformylation is accompanied by double bond hydrogenation, and mono-oxygenated derivatives are produced in lower yields than with monounsaturated substrates (4). However, with the rhodium-triphenylphosphine catalyst, hydroformylation of polyunsaturates produces polyformyl derivatives in high yields (6,8,9). Various rhodium-derived polyfunctional oxo products proved useful in coating (10), urethane foam (11-13), plasticizer (14,15), and lubricant (16) applications.

One advantage of the cobalt carbonyl system, besides lower catalyst cost, is that it forms difunctional products from polyunsaturated fatty substrates which may be desirable in certain polymer applications. Also, these oxo products can be reduced to hydroxymethyl derivatives with cobalt carbonyl (4), but not with rhodium-triphenylphosphine when a hydrogenation catalyst, such as nickel, is required (5). Finally, cobalt-carbonyl oxo technology is well advanced in the petrochemical field, and continuous processes are used commercially (17,18).

Cobalt carbonyl catalysis was reinvestigated to determine if useful oxo derivatives can be prepared in high yields and to explore ways of recycling the catalyst. This paper reports two promising approaches to the high-yield preparation of potentially useful oxo products from fat derivatives.

EXPERIMENTAL PROCEDURES

Materials, analytical methods, hydroformylation procedures, and preparation of derivatives have been described previously (4,5,8). Different work-up procedures were used for different oxo products.

Formyl Derivatives

Hydroformylation of methyl oleate at 120 C in the absence of MeOH (Table I, run 2) produced formyl esters, which were converted to the dimethyl acetals (DMA) by treating crude reaction mixtures with HCl-MeOH in the presence of trimethylorthoformate (14). After neutralization (aqueous Na_2CO_3), a large portion of solid metallic cobalt precipitated. Almost all the MeOH was removed with a rotating evaporator under vacuum; then the residue was taken up in diethyl ether and water and transferred into a separatory funnel. As the lower aqueous layer was pink, it contained the rest of the soluble cobalt catalyst. As the DMA product after water washing and drying (Na_2SO_4) was colorless, presumably it was free of cobalt.

The DMA esters produced directly by hydroformylation in the presence of MeOH (Table I, runs 4,5, and 12) could not be distilled directly because the enol ether of methyl formylstearate (15) was formed by thermal cracking in the presence of residual cobalt catalyst. Decomposition of the cobalt catalyst with dilute HCl (4) resulted in hydrolysis of the DMA esters to the formyl derivatives. The best procedure consisted of treating the crude product with aqueous Na_2CO_3, stripping off the MeOH, and extracting the DMA esters with diethyl ether. The cobalt catalyst remained in the water layer as a pink solution.

Hydroxymethyl Derivatives

Hydroformylation of methyl oleate at 180 C (Table I, run 8) produced hydroxymethyl esters, which were worked up with dilute HCl to decompose the cobalt carbonyl catalyst (4). In another procedure, hydroxymethyl esters were made by first hydroformylating at 120 C (to form formyl esters mainly) and then hydrogenating with the same cobalt carbonyl catalyst at 180 C (Table I, run 9). By this two-step procedure, metallic cobalt was precipitated in the final reaction mixture and easily filtered off from a benzene solution of the mixture. This precipitated cobalt proved catalytically active under hydroformylation conditions.

RESULTS AND DISCUSSION

Various oxo products were converted to suitable derivatives, which can be distilled and analyzed by gas-liquid chromatography (GLC). Formyl products obtained predominantly at 110-120 C (Table I) were converted to DMA esters, which could be distilled in good yields in the absence of cobalt carbonyl catalyst. However, if this catalyst was not completely removed, substantial amounts of enol ether (15) were formed during distillation. This by-product was detected by IR (1050, 1070, 1110 cm^{-1}) and by GLC with methyl 9(10)-methoxymethylenestearate (15) as the reference.

Hydroxymethyl products obtained predominantly at 180 C (Table I) were converted to various derivatives to determine which were most suitable for distillation. The distillation yields were highest after saponification, methylation, and acetylation (Table II). The lower yields from direct acetylation (oleate product) or from methylation followed by acetylation (oleic acid product) can be attri-

TABLE I

Cobalt Carbonyl Catalysis[a]

Run no.	Substrate	Solvent	Co-catalyst	Temperature (C)	H_2:CO	Time (hr)	Distillable product (%) (derivative)	Gas-liquid chromatographic analysis[b] (%) Sat	Un	Formyl	HOMe	DMA
1	MeOl	Toluene	None	110	1:1	6.5	Not run	4.6	24.9	56.1	7.2 + 7.2[c]	----
2	MeOl	Toluene	None	120	1:1	2.5	95.4 (DMA)	4.4	0.0	79.1	15.6 + 0.9[c]	----
3	MeOl	Toluene	MeOH[d]	120	1:1	5	86.8 (DMA)	5.5	0.0	10.7	----	76.8 + 7.0[c]
4	MeOl	MeOH	None	120	1:1	3.5	97.2 (DMA)	4.7	0.0	18.9[e]	----	71.4 + 5.0[c]
5	MeOl	MeOH	TMOF[d]	120	1:1	2	96.5 (DMA)	6.5	0.6	7.1	----	76.4 + 9.3[c]
6	MeOl	Toluene	None	150	1:1	2	Not run	6.8	0.5	31.6	61.1	----
7	MeOl	Toluene	Benzo CN[f]	150	1:1	6	Not run	5.4	1.4	61.4	31.7	----
8	MeOl	Toluene	None	180	2:1	2	75.0 (OAc)[g]	13.3	1.7	0.0	74.5 + 10.5[c]	----
9[h]	MeOl	None	None	120	1:1	1.5		3.5	4.1	77.4	15.0	----
				180	1:0	1	83.0 (OAc)	3.5	0.0	0.2	85.0 + 11.3[c]	----
10	MeOl	None	Used catalyst[i]	180	2:1	1		8.6	8.2	62.1	17.7 + 3.4[c]	----
				180	1:0	0.5	Not run	8.6	2.1	64.3	19.6 + 5.4[c]	----
11	Ol acid	Toluene	None	120	1:1	2	96.2 (Me-DMA)	7.4	1.6	63.4	18.4 + 9.2[c]	----
12	Ol acid	MeOH	None	120	1:1	3	98.7 (DMA)	4.6	0.0	3.2	----	88.5 + 3.7[c]
13	Ol acid	Toluene	None	180	2:1	3	56.8 (Me-OAc)[g]	16.6	2.5	3.8	77.1	----
14	MeSFO	Toluene	None	110	1:1	6	Not run	13.3	0.0	54.0	32.7	----
15	MeSFO	Toluene	None	180	2:1	2	86.5 (Me-OAc)	15.6	0.0	0.0	84.9	----
16	MeLSO	Toluene	None	120	1:1	3	82.0 (DMA-OAc)	13.7	0.0	26.6	59.6	----
17	MeLSO	MeOH	None	120	1:1	6	89.2 (DMA-OAc)	9.7	0.0	4.0	----	86.3
18[h]	MeLSO	None	None	120	1:1	2.5						
				180	1:0	2	67.0 (OAc)	15.2	0.0	0.0	84.8	----
19	LSO	None	None	180	2:1	2.5	87.6 (Me-OAc)	20.2	0.0	1.3	78.5	----

[a] Key to abbreviations: MeOl = methyl oleate, Ol acid = oleic acid, MeSFO = methyl safflower esters, MeLSO = methyl linseed esters, LSO = linseed oil, TMOF = trimethylorthoformate, Benzo CN = benzonitrile, DMA = dimethyl acetal, OAc = acetate, Me = methyl, sat = saturates (runs 1-13: stearate, runs 14-19: palmitate + stearate), un = unsaturates, HOMe = hydroxymethylstearate. 0.5 mol $Co_2(CO)_8$ per 100 mol oleate or polyunsaturates (5.8 wt %), total volume of reaction mixture 100 ml (50 g substrate used with solvent, 110 g substrate without solvent), autoclave: 250 ml rocker-shaker type.

[b] On a JXR column programmed at 160-260 at 4 C/min (8).

[c] Linear isomers (1,18-disubstituted) identified on basis of previous work (4).

[d] Same molar concentration as methyl oleate (0.17 mol).

[e] Includes 2.5% enol ether (15).

[f] Same molar concentration as cobalt carbonyl (0.0073 mol).

[g] Higher yields obtained by different derivatization procedures (Table II).

[h] Two-step procedure: hydroformylate with H_2:CO; replace synthesis gas with H_2.

[i] From run 9 (1.5 g/110 g substrate).

TABLE II

Analysis of Cobalt Carbonyl Oxo Derivatives

Run no.[a]	Substrate[a]	Derivatization[b]	Distillable product (%)	Gas-liquid chromatographic analysis[c] (%)			
				Sat	Un	Formyl	Acetyl[d]
8	MeOl	OAc	75.0	10.4	0.0	0.0	79.5 + 10.1
		Me-OAc	91.4	9.3	0.5	0.0	78.7 + 11.5
		Sap-Me-OAc	95.0	8.0	0.8	0.0	78.7 + 12.5
13	Ol acid	Me-OAc	56.8	5.5	2.3	3.0	80.9 + 8.3
		Sap-Me-OAc	89.5	7.6	1.1	3.3	78.6 + 9.4

[a] See Table I. MeOl = methyl oleate, Ol acid = oleic acid.

[b] OAc = acetylated, Me = methylated, Sap = saponified. See ref. 4 for procedures. Methylations were done by refluxing with MeOH containing 1% H_2SO_4 for 2 hr.

[c] On a JXR column programmed at 160-260 at 4 C/min (8).

[d] Linear isomers (1,18-disubstituted) identified on basis of previous work (4).

buted to the presence of nondistillable estolides formed by hydroformylation at high temperatures. Previous work showed that under these conditions estolides and other by-products are formed by cobalt carbonyl-catalyzed hydroformylation (2-4).

In products containing substantial amounts of both formyl and hydroxymethyl esters, derivatization into materials suitable for distillation was not too successful. Some products were first converted to DMA esters and then acetylated. However, IR studies indicated loss of OH functionality (3500 cm^{-1}) after acetalization with acidic MeOH. When acetylation was carried out on formyl products, CHO functionality (2700, 1740 cm^{-1}) was lost. It is known that aldehydes interfere with conventional acetylation by acetic anhydride-pyridine when used for the analysis of hydroxyl groups (19). DMA esters would also be expected to interfere (14). Therefore, distillation yield data are not reliable for those derivatives of products containing large amounts of both formyl and hydroxymethyl esters.

Table I summarizes reaction conditions and main oxo products from methyl oleate, oleic acid, safflower and linseed methyl esters, and linseed oil. Formylstearate produced directly at 120 C from methyl oleate (79%) and formylstearic acid from oleic acid (63%) were 95-96% distillable as the DMA esters. However, they were mixed with varying amounts of hydroxymethyl derivatives (Table I, runs 2 and 11). In the presence of either a stoichiometric amount (run 3) or excess MeOH (run 4), the DMA ester formed as major product was mixed with 7-19% formyl ester. Addition of trimethylorthoformate improved the conversion to DMA ester and accelerated the rate (run 5). This observation agrees with a similar report (20) on the use of alcohols and orthoformic esters under hydroformylation conditions to decrease side reactions and the reduction of aldehydes by formation of fairly stable acetals. With oleic acid, the DMA methyl ester was produced directly in good yield (run 12).

The hydroxymethylstearate (87% by GLC) produced by hydroformylation in one step at 180 C from methyl oleate was only 75% distillable as the acetate derivative (run 8). With oleic acid, more stearate was formed than with methyl oleate, and the product was only 57% distillable as the acetate methyl ester derivative (run 13). Yields of hydroxymethyl esters were improved by carrying out the hydroformylation in two steps: hydroformylating first at 120 C to form the formyl esters, then hydrogenating by replacing the synthesis gas with H_2, and raising the temperature to 180 C. The final product was 83% distillable as acetates (run 9). The catalyst, which decomposed under these conditions, was readily separated by filtration. This cobalt catalyst was inactive at 120 C but active at 180 C (run 10). When this recycled catalyst was used, the product contained more formylstearate (64%) than hydroxymethylstearate (25%). Hydrogenation following hydroformylation increased the proportion of hydroxymethyl esters only 4%.

Much work has been reported in the hydrocarbon field on modified cobalt carbonyl to improve catalyst stability and selectivity for certain oxo products (21). On the one hand, the yield of alcohols is increased by adding alkylphosphines to the cobalt carbonyl catalyst (22). On the other hand, the yield of aldehydes is increased either by using less stable arylphosphite complexes of cobalt carbonyl (23) or by adding to cobalt carbonyl such complexing agents as nitriles, anisole, thioanisole, or thiophenol (24). Tributylphosphine increased the proportion of linear isomers produced from oleate and linoleate, but lowered yields of distillable oxo products (4). Since benzonitrile proved to be the most effective modifying agent on the stoichiometric hydroformylation with cobalt carbonyl (24), its effect was investigated on the catalytic hydroformylation of methyl oleate. Although this complexing agent inhibited hydroformylation at 110 C, it was effective in increasing the proportion of formyl products at 150 C (Table I, compare runs 6 and 7).

Included in Table I are product distributions from hydroformylated polyunsaturated substrates. At 120 C, linseed methyl esters produced a higher proportion of hydroxymethyl esters than did methyl oleate (compare runs 16 and 2). Distillation yields of DMA esters produced directly or after acetylation were lower than corresponding products from methyl oleate (compare runs 16-17 with runs 2 and 4). Similarly, yields of distillable hydroxymethyl esters were lower with linseed methyl esters by the two-step hydroformylation-hydrogenation procedure than with methyl oleate (compare runs 18 and 9). With linseed oil, distillation yields of hydroxymethyl esters were better because the products had to be saponified and converted to acetoxy methyl esters. Previously, we (4) showed that by-product formation lowers the yields of oxo products from polyunsaturates. However, we now find that saponification improves these yields after converting the hydroxymethyl acids to the acetoxymethyl esters.

This work provides the basis for two improved and promising cobalt carbonyl oxo processes yielding potentially useful products from fatty derivatives. In one process, hydroformylation with MeOH at 120 C produces fairly stable DMA esters from both methyl oleate and oleic acid. This dimethyl acetal is useful as a secondary polyvinyl chloride (PVC) plasticizer (15). It is also an intermediate in preparing pentaerythritol cyclic acetal of formylstearate, a useful monomer for preparing poly(ester-acetals) and poly(amide-acetals) (15). In the two-step process, hydroformylation followed by hydrogenation improves the yield of hydroxymethyl esters from both mono- and polyunsaturated fatty substrate. The cobalt catalyst could be recylced by this second process. The acetoxymethyl derivatives of these oxo products have been used as PVC plasticizers (25).

The oxo products made offer many areas of practical interest (1). Although the basis for catalyst recycling processes is described, larger scale operations and continuous operation need to be explored.

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