

Recovery of Solubilized Rhodium from Hydroformylated Vegetable Oils and Their Methyl Esters

E.J. DUFEK and G.R. LIST, Northern Regional Research Center, ARS, USDA, Peoria, IL 61604

ABSTRACT AND SUMMARY

Procedures were developed to extract rhodium from hydroformylated vegetable oils and methyl esters. Among the numerous reagents surveyed, aqueous hydrogen cyanide with triethanolamine (TEA) was found to be most effective. The effects of time, temperature, and concentration of reagents were studied. Over 98% of the solubilized rhodium was removed from crude methyl formylstearate at 100 C for 1 hr with 0.5% hydrogen cyanide, 5% water, and 0.5% TEA. Over 98% of the solubilized rhodium was also extracted from hydroformylated soybean and safflower methyl esters; however, 1% hydrogen cyanide, 10% water, and 0.62% TEA had to be used. Only 90% of the rhodium was removed from hydroformylated soybean oil. The reagents used can be adapted to a continuous extraction procedure.

INTRODUCTION

Hydroformylation (oxo reaction) of unsaturated fatty esters and vegetable oils using a homogeneous rhodium-triphenylphosphine or triphenylphosphite catalyst has been studied extensively at the Northern Regional Research Center (1-4). The oxo reaction involves treating an unsaturated oil with carbon monoxide and hydrogen in the presence of a Group VIII catalyst. The unsaturated group adds carbon monoxide and hydrogen, and depending on conditions and nature of the complexed metal catalyst the products are alcohols, aldehydes, and acids. However, during this process, the supported rhodium catalyst is partially solubilized by the substrate. A process for recovery and reuse of the high-cost rhodium catalyst used in preparation of methyl formyl and carboxystearate recently has been shown to be commercially feasible (4,5). This process, however, uses a molecular distillation (with some decomposition) to purify the fatty products and concentrate the solubilized rhodium in the tarry residue for recovery. The tarry residues are then calcined at 600 C to reactivate the catalyst (4). The high boiling hydroformylated products are usually used as intermediates and, therefore, need not be purified extensively. An extraction procedure which eliminates the distillation for recovery of solubilized rhodium catalyst for reactivation by calcining is now reported.

EXPERIMENTAL PROCEDURES

Starting Materials

Methyl formylstearate (MFS), hydroformylated soybean and safflower methyl esters, and hydroformylated soybean oil were prepared with freshly calcined rhodium on alumina-triphenylphosphite catalyst as previously described (1-4). The products were filtered through paper and/or fine sintered glass.

Hydrogen cyanide (HCN) was prepared as described (6), redistilled, and then weighed and diluted to make a 25% aqueous solution (fume hood). The aqueous HCN solution was stored in a dry ice-acetone bath. Aqueous HCN was pipetted as needed into the various amines and added immediately to the weighed MFS in the pressure vessel.

Additional water was added to total the concentration shown in the tables.

Extraction of Rhodium from Hydroformylated Fatty Esters and Oils

Preliminary survey of procedures and reagents: MFS (15 g) and the various reagents used were weighed into a stoppered 50-ml Erlenmeyer flask. The contents were heated on a steam bath and stirred magnetically. Small samples were taken periodically and centrifuged. Crude MFS and the centrifuged extracted sample [100 mg/25 ml methyl isobutyl ketone (MIBK)] were analyzed for rhodium by the direct method as described (7). Some of the various reagents and amounts used and percent Rh removed are shown in Table I.

Extractions in pressurized vessel: MFS (80 g) and the reagents were placed in a 300 cc, 316 SS Magne-drive pressure vessel. Aqueous-HCN when used was pipetted into and dissolved in the basic reagent before addition to the MFS. The vessel was flushed briefly with nitrogen and pressurized to 10-20 psi. Samples were taken periodically and analyzed by atomic absorption spectrometry (7). The results are shown in Tables II-IV.

RESULTS AND DISCUSSION

Numerous patents describe procedures for recovery of spent rhodium catalysts from oxo reactions. Most procedures, however, recover the rhodium from viscous tarry distillation residues by adsorption using magnesium silicate (8) or basic ion exchange resins such as Amberlite 21A (9,10), reduction with zinc dust (11) or sodium borohydride (12), and extraction with sodium hydroxide and cyanide (13) or aqueous nitric acid-hydrogen peroxide (14). Rhodium also has been recovered from high boiling residues by extraction at 600 psi ethylene and 75% aqueous sulfuric acid (15).

Only a few references list methods for recovery of rhodium directly from crude hydroformylated products, and the amounts of rhodium removed usually were low; for example, only 82% was recovered when diformyltricyclodecane was refluxed with 10% aqueous acetic acid (16). A continuous process using steam at high temperature and pressure has also been reported (17).

For the preparation of hydroformylated products, especially fatty acid glycerides which cannot be distilled, an ideal system for extraction of rhodium catalyst is one which requires small amounts of reagents. Further, inorganic salts must be avoided to prevent a buildup of salts in the repeated calcining process for reactivation of rhodium catalyst (5).

In this work, the direct method of analysis of 100-mg samples in MIBK (7) was used to determine rhodium solubilized in hydroformylated fatty esters. In procedures where the direct method of analysis indicated over 85-90% removal, analysis of a 5-g sample by the rapid sulfuric acid digestion procedure (7) was also carried out. The results agreed favorably.

Preliminary Tests

Hydroformylated fatty esters and glycerides prepared with rhodium catalysts contain approximately 300 μ g of

TABLE I

Survey of Reagents for Extraction of Fat Solubilized Rhodium^a

Reagent	W %	% Extracted
Water	20 ^b	32
Hydrochloric acid	5-10	53
Phosphoric acid	5-10	19
Sulfuric acid	0.2 ^c	52
Citric acid	1.0 ^d	31
Oxalic acid	1.0 ^d	29
Carbon dioxide	20 ^e	34
EDTA	2.5 ^f	21-67
Hexamethylene diamine	1.0 ^d	0
Ammonia	4-10	78-90
Ammonium carbonate	0.5 ^g	36
Ammonium carbonate	1.0 ^{d,h}	52-75
Ammonium thiocarbonate	1.0 ^d	30
Pyridine	1.0 ^d	60
Morpholine	1.0 ^d	79
Triethylamine	1.0 ^{d, 7d}	88,90
Acetylacetone	1.0 ^d	80
Hydroquinone	1-5 ^g	35-73
Acetonitrile	1.0 ^d	20
Glycerol	1.0 ^g	46

^aCarried out on 15 g product at 100 C in a 50-ml stoppered Erlenmeyer flask with magnetic stirring.

^bThree extractions.

^cIn 5 ml water.

^dWith 20 wt % water.

^eSaturated aqueous solution at room temperature.

^fEDTA = Ethylenediamine tetraacetic acid, 2.5 wt % with varied amounts (2-5 wt %) of morpholine or triethanolamine and H₂O.

^gNo solvent.

^hWith 4 wt % methanol.

solubilized rhodium per gram of oil. Initial attempts to use acidic and basic forms of ion exchange resins such as Amberlite IR45, Dowex A-1, and Dowex WX8 resulted at best in only 34% Rh removal (acidic Amberlite IR45) from MFS. Carbon black absorbed rhodium and the first fractions were free of Rh, but the carbon packing flooded rapidly and succeeding fractions contained increasing amounts of Rh.

A survey of procedures and reagents for the extraction of solubilized Rh from MFS (15 g) was first carried out in

TABLE II

Extraction of Rhodium from Methyl Formylstearate^a Using Selected Amines

Reagent	HCN ^b (wt %)	Temp. (C)	Removed ^c (%)
Ammonia		25	34
Ammonia		100	50
Ethanolamine		100	22
Diethanolamine		100	49
Triethanolamine		25	61
Triethanolamine		100	68
Ethanolamine	0.5	100	76
Diethanolamine	0.5	100	95
Triethanolamine	0.5	100	96 ^d
Triethanolamine	0.5	100	98-99

^aPressurized vessel, 80 g methyl formylstearate under 5-10 psi nitrogen, 1.25 wt % reagent and 5 wt % H₂O.

^bHCN = Hydrogen cyanide

^cAfter 4-hr reaction.

^dAfter 1/4 hr.

50-ml stoppered Erlenmeyer flasks. The results of some extractions with various reagents are shown in Table I. Later, 80 g of MFS were treated in a 300-ml Magedrive pressure vessel (Autoclave Engineers, Erie, PA). As expected, extractions in the pressure vessel were more efficient. Generally, extractions of crude MFS with aqueous acids removed less than 50% of the dissolved rhodium. In basic media, over 60% was extracted. The only exception was hexamethylenediamine where 0% was removed. Varied results from 20 to 80% were obtained when compounds such as glycerol, hydroquinone, and acetylacetone were used for the extraction. Triethylamine (Table I) is more efficient (88-90%) in extracting rhodium than triethanolamine (TEA) (Table II), but triethylamine forms emulsions with MFS that break slowly on standing. This was not a problem with TEA.

The results of some extractions of MFS with ammonia and mono, di-, and triethanolamines in a pressurized vessel (300 cc Magedrive with 10 psi nitrogen) are shown in Table II. Extractions with all reagents both acidic and basic except ammonia (Tables I, II) resulted in nearly complete recovery of MFS. With ammonia, however, large amounts

TABLE III

Effect of Time on Extraction of Fat^a Solubilized Rhodium

Extraction condition							
Temperature (C)	100	100	100	100	100	50	100
Reagent (wt %)							
TEA ^b	1		1	1		1	1
H ₂ O		4	4	4	5	5	5
HCN					0.5	0.5	0.5
TPP ^b				1			
Rhodium extracted (wt %)							
Time (hr)							
1/4	—		36	25	—	—	97.2
1/2	—		49	—	—	—	—
1	9		70	36	89	78	98.1
2	23		75	59	—	82	—
3	35 ^c		80	75	—	84	—
4		67	86	80	90	88	98.3
5		73	90 ^d	82			98.3
6		77					

^aCrude filtered methyl formylstearate (hydroformylated methyl oleate) contained 304 µg Rh/g.

^bTEA = triethanolamine, TPP = triphenylphosphite, HCN = hydrogen cyanide.

^cWater added and the reaction continued for 3 more hr.

^dDirect analysis in methyl isobutyl ketone (MIBK) (90.4%). Sample ashed with sulfuric acid (90.5%).

TABLE IV

Effect of Concentration of Reagents
on Extraction of Rhodium from Methyl Formylstearate (MFS)

HCN ^a (wt %)	Reagent		Rh removed ^b (%)
	H ₂ O (wt %)	TEA ^a (wt %)	
0.25	4	0.62	98.4
0.50	4	0.62	98.3
0.75	4	0.62	98.0
0.25	4	1.25	96.8
0.50	4	1.25	98.7
0.75	4	1.25	97.4
0.25	6.2	0.62	97.3
0.50	6.2	0.62	97.1
0.75	6.2	0.62	97.9
0.50	6.2	1.25	97.6
0.75	6.2	1.25	97.4
0.50	20	0.62	93.7
0.50	10 ^c	0.62	97.9

^aHCN = hydrogen cyanide; TEA = triethanolamine.

^bAt 100 C for 1 hr; 80 g MFS in pressurized vessel.

^cMethanol-water, 50:50 v/v for 2 hr.

of voluminous precipitates were produced resulting in large losses of MFS.

Extractions with Ethanolamines and HCN

Mono-, di-, and triethanolamine extracted 49, 61, and 68%, respectively, of the rhodium present. Addition of hydrogen cyanide to the three ethanolamines increased the amount removed from 76 to 98-99%. Water is necessary with TEA. As shown in Table III, reaction for 3 hr with only TEA removed 35% Rh. At this point, water was added and after an additional hr at 100 C, the amount of Rh removed was increased to 67%. Recovery of up to 80-90% was observed by addition of HCN or triphenylphosphite (Table III). Of the various reagents tested, aqueous TEA-HCN at 100 C for 1 hr was found to be the most efficient for the extraction of Rh from MFS, although 97.2% was recovered in only 15 min. This percentage changed only slightly in 5 hr to 98.3%. At 50 C, only 88% was recovered in 4 hr. Based on these results, various concentrations of HCN-H₂O-TEA were studied (Table IV). Only small variations were noted. At concentrations of 0.5:4:1.25%, respectively of HCN:H₂O:TEA, 98.7% of the Rh was recovered. Aqueous methanol (50-50 v/v) at 10% level with hydrogen cyanide and TEA also extracted 97.9%, whereas 20% water lowered the recovery to 93%. A second extraction with HCN-H₂O-TEA removed additional Rh from MFS. Thus, these reagents and procedure at 100 C could be adapted readily for use in a continuous extraction apparatus.

Attempts to extract Rh with HCN-H₂O-TEA from MFS which was not filtered to remove spent catalyst were unsuccessful (0% Rh recovery). The used Rh-alumina catalyst, therefore, must be removed by filtration before treating the crude MFS to recover the fat-solubilized rhodium.

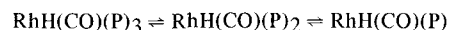
Extraction of rhodium from hydroformylated soybean and safflower methyl esters required additional amounts of reagents. To obtain 98 (1 hr) to 99% (2 hr) Rh recovery, concentrations of 1:10:0.62% respectively, of HCN:H₂O:TEA had to be used.

Hydroformylated soybean oil containing 286 μg Rh/g when treated with 1:10:0.62% HCN-H₂O-TEA at 100 C for 1 hr produced viscous emulsions that failed to break in 24 hrs. However, after adding ether and washing with a 50:50 methanol-water mixture, the hydroformylated soybean oil contained 37 μg Rh/g (87.1% recovery).

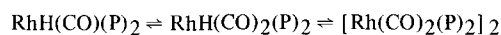
Although the use of inorganic salts is not desirable because of their buildup during the calcining or reactivation of the rhodium catalyst (5), aqueous sodium cyanide and bicarbonate solutions were effective in removing Rh from

MFS. For example, saturated sodium bicarbonate removed 91% and 0.5% NaCN and 5% H₂O in 1 hr at 100 C removed 98.5% of the Rh present in MFS. A similar run using methyl carboxylstearate [air oxidized MFS (5)] and aqueous sodium cyanide resulted in 90% recovery of the rhodium present.

The exact structure of the various homogeneous rhodium-triphenylphosphine or phosphite complexes can be postulated but is not definitely known, thus adding to the problems of extraction. The higher oxidized states of the rhodium catalyst present in the reactivated calcined catalyst (4), in the presence of H₂, CO, and triphenylphosphine or phosphite, certainly must be reduced to rhodium (I) and form known active complexes with π-binding ligands. These complexes, studied by several investigators (18,19), form an equilibrium mixture in benzene



where P = phosphine compound. Depending on temperature and pressure of H₂ and CO, active hydrogenation and hydroformylation complexes such as



are also formed (18).

The stability and solubility of the various complexes in aqueous acids would vary and give results shown in Table I. Repeated extractions only slightly enhanced the amount of Rh removed from the hydroformylated products. In basic media, however, the Rh complex involves nitrogen ligands and certain complexes would be expected to be more soluble. In aqueous-TEA-hydrogen cyanide systems at 100 C, the Rh (I) probably is oxidized to a single species similar to [RhH(CN)₄(H₂O)]⁻² previously reported (20). The possible hybrids and aqueous Rh(CN)₄(TEA) complexes or ions are intriguing and should be studied further.

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