Hydrogenation of Carboxylic Acids and Synergistic Catalysts

BHUPENDRA C. TRIVEDI, DACE GROTE and THOMAS O. MASON,
Ashland Chemical Co., PO Box 2219, Columbus, OH 43216

ABSTRACT

Rhenium heptoxide, a known catalyst for hydrogenation of carboxylic acids to alcohols, forms synergistic combinations with palladium, platinum, rhodium and ruthenium catalysts. This effect is also seen at lower presures (500 psi). Synergism is also mainfest when rhenium and palladium (or rhodium) are used as supported catalysts on silica and used in a flow mode. An interaction of unknown nature between the metals suggests itself. The process is not very efficient at lower pressures giving lower conversion in the flow mode. At higher temperatures needed for higher rates, significant participation of side reactions such as decarboxylation of the acid and hydrogenolysis of the alcohol occurs yielding hydrocarbons.

INTRODUCTION

Among the first commercial syntheses of fatty alcohols was one from the corresponding acid or ester. Le Blanc reduction of esters using sodium metal and alcohol (1) soon had to give way to a more economical catalytic route. The latter employed copper chromite or similar catalysts and required high temperatures and pressures (2,3). Alternate routes to fatty alcohols such as oxo alcohols (4) and Ziegler alcohols (4) were discovered. However, there are some compounds, such as oleyl alcohol, for which neither of the above is satisfactory.

Commercial hydrogenation of fatty acid or ester requires 250-300 C and 3000-4000 psi (2,3). Such severe conditions necessitate high capital cost making a search for a process using lower pressure and temperature highly desirable.

Platinum metals are not particularly noted for their ability to hydrogenate carboxylic acids (5). Fischer et al. (6) have reported Ru/C to be effective with perflurocarboxylic acids. Similarly, glycolic acid has been easily reduced at 1500 psi with RuO_2 catalyst. However the same catalyst requires 7000 psi for acetic acid (7). Rh_2O_3 has been shown by Grimm to be an active catalyst at 150 C and 2000 psi (8).

Rhenium heptoxide has been shown by Broadbent (9) to be an excellent catalyst for the hydrogenation of fatty acid at 170 C and 200 atm. The efficient reduction of acids was attributed to "rhenium black" or "ReO_2" depending on the solvent used. It was also concluded that addition of trace amounts of other "extrinsic reducing agents" such as PtO_2, Ru/C and Norit had little or slightly negative effect.

With the above information on hand, our objective was to find efficient catalysts for the hydrogenation of acids which could also be employed at lower pressures.

EXPERIMENTAL

Autoclave Approach

A 300 ml Magnedrive autoclave (Autoclave Engineers, Erie, PA) was charged with the acid, catalyst, solvent and any other reagent as needed, and sealed. The unit was flushed three times with hydrogen before pressurizing and heating. When at temperature, the system was brought to desired pressure and any consumed H_2 was refurnished. Samples were taken intermittently.

Continuous Approach

The reactor was a 12 in. × 1/2 in. 304 S.S. tube filled with catalyst. The effective volume of the reactor and hence catalyst load was ∿18 ml. Heatup and equilibration were performed with acid and H_2 flow present. Samples were taken from the reservoir periodically. Distilled octanoic acid was used as a feed.

Catalyst Preparation

For the Re + M (M = Pd, Rh) on SiO_2, the catalysts were prepared by mixing soluble salts of the metals in water with 100-200 mesh silica gel. The water was evaporated on a roto-vap, followed by drying in a 110 C oven. Catalyst activation involved the following sequence of reductions under H_2: (a) heating gradually from room temperature to 200 C; (b) heating in steps of 50 C while maintaining at that temperature for 30 minutes; (c) maintaining at 400 C for three hours; and (d) cool-down under a flow of H_2.

TABLE I

Effect of Bimetallic Catalysts (170 C, 2500 psi, 1,4-Dioxane Solvent[a])

Expt.	Cat	Cat (g)	Cocat	Cocat (g)	Time (hrs)	Analysis %		
						Acid	alcohol	Ester
1	Re_2O_7	0.26		–	6	21.2	48.1	30.7
2		0.13	5% Ru/C[b]	1.0	3	trace	84.0	16.0
3			5% Rh/C[c]	0.8	4	0	76.7	23.3
4			Raney Ni	0.2	5	57.8	16.9	25.3
5			G49B(Ni)[d]	1.0	4	95.4	0.5	4.1
6			$CuCO_3$	0.025	3	89.1	1.8	9.1
7			5% Pd/C[b]	1.6	5	13.3	62.2	24.5
8			5% Pt/C[b]	1.6	5	15.4	60.3	24.3
9			G61Rs(Co)[d]	1.0	4	90.7	1.4	7.9
10			Norit	1.0	3	73.0	6.9	20.1
11	–	–	5% Ru/C[b]	2.0	8	34.7	30.7	34.7
12	–	–	5% Rh/C[c]	1.6	5	90.7	1.2	8.1

[a] Typical reaction consisted of 28.8 g octanoic acid; 28.8 g 1,4-dioxane; 5.0 g water and catalysts.
[b] 50% wet.
[c] 20% wet.
[d] Girdler catalysts.

The catalyst (60-80 mesh) obtained by sieving was employed for the hydrogenation.

Analysis

For the autoclave run, gas liquid chromatography (GLC) without internal standard was used.

For the monitoring of the flow reactor, GLC with an internal standard was performed using a 10 ft. × 1/8 in. UCW-98 on Chromosorb W column. Acid did not respond well on the column, and hence acid was separately determined by titration.

Conversions and selectivity to alcohol were calculated so that the alcohol and the acid present in the combined form as ester can be accounted for. The following equations were used:

$$\text{Conversion} = 100\ [0.5624\ (\%\ \text{ester}) + \%\ \text{acid}]$$
$$\text{Selectivity} = 0.5078\ (\%\ \text{ester}) + \%\ \text{alcohol}] \times 100/\%\ \text{Conv. Acid}$$

RESULTS AND DISCUSSION

Rhenium heptoxide was verified as a catalyst under Broadbent conditions (9). However, it was observed that on adding close to equivalent amount of Ru/C, in situ, the rate of hydrogenation increased significantly. On further examination, other catalysts such as Pt/C, Pd/C, Rh/C also were found to have a rate-enhancing effect, although to a lower degree (10,11). In Table I, data on high pressure (2500 psi) hydrogenation were reported. Note that for the study of cocatalysts, one-half the quantity of each as an individual catalyst is employed. Figure 1 compares rates due to rhenium heptoxide with those of the reaction promoted by Ru/C. Judging from Figure 1 and data in Table I, it was obvious that we were observing a "synergism" in progress. Since a number of catalysts were examined in their "supported on carbon" form, the effect of the support had to be known. The experiment with Norit confirmed that the rate enhancement was not due to the high surface area of the support. Other cocatalysts such as nickel, cobalt and copper were examined under the reaction conditions. Each seemed to have a deleterious effect on the rate of hydrogenation produced by Re_2O_7 alone.

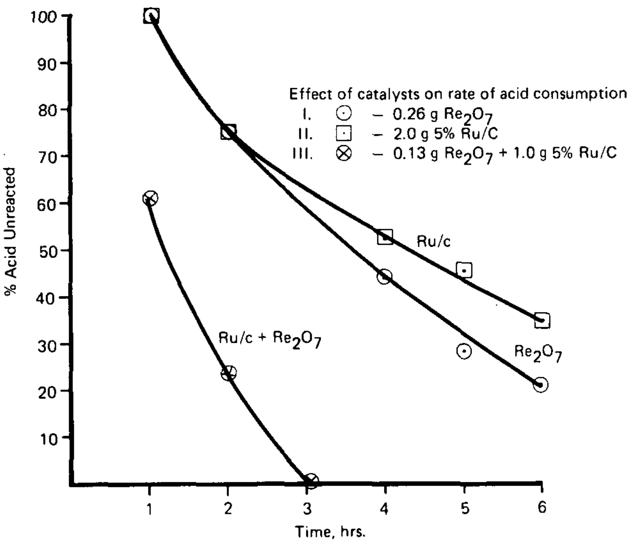

FIG. 1. Hydrogenation of 0.2 mole octanoic acid at 170 C, 2600 psi.

Since the primary objective was to find a low pressure hydrogenation catalyst, evaluation at lower pressures was initiated. With Re_2O_7 + Ru/C catalyst, an excellent reaction was observed at 200 C and $\sim$600 psi total pressure. However, attempts to repeat this run invariably produced a

TABLE II

Low Pressure Hydrogenation Effect of Catalyst Concentrations

Expt. (#)	Acid (moles)	Catalyst $\times 10^{-4}$ gram atoms Re	Pd	Temp. (°C)	Pressure (psi)	Acid	Analysis % Alcohol	Ester	Hydrocarbon
13	0.2	5.4	3.7	200	500	53.7	16.0	30.3	0.0
14	0.2	5.4	7.4	200	500	36.7	26.5	34.3	2.4
15	0.2	10.8	7.4	200	500	29.7	32.8	34.6	2.9
16	0.2	10.8	7.4	230	800	18.6	5.7	35.6	40.1

For reaction mixture see Table I.
Reaction time—5 hr.

TABLE III

Flow Hydrogenation of Octanoic Acid with Re + Pd on Silica[a]

Cat. wt% Re	Pd	(°C)	% Distribution Hydrocarbon	Alcohol	Acid	Ester	Acid conv %	Selectivity[b] Heptane	Octane	Alcohol
4.7	–	200	0.4	1.1	82.0	14.2	10.0	1.3	2.6	83.0
4.7	–	230	2.2	0.8	80.2	14.5	11.7	14.0	4.6	70.0
4.6	2.3	200	1.7	15.3	34.2	48.3	38.6	2.1	2.3	103.0
4.6	2.3	230	12.8	26.4	27.2	27.2	55.9	17.3	5.6	74.6
4.5	4.5	200	1.9	32.4	12.4	50.6	59.1	2.0	1.4	98.2
2.4	2.4	200	0.7	4.5	54.4	38.6	23.8	1.8	1.3	101.1
2.4	2.4	230	17.6	21.5	25.2	31.4	57.2	24.6	6.2	65.3
2.3	4.6	200	0.7	3.4	58.7	34.6	21.8	2.3	0.9	96.0
2.3	4.6	230	26.8	14.2	30.3	28.0	53.9	46.4	3.4	52.8

[a] Conditions: pressure 300 psi, acid ≅ 18 ml/hr, H_2 18-19 lit/hr measured at atmospheric pressure.

[b] At very high and very low concentrations, accuracy of analysis suffers significantly; hence, total does not equal 100%.

TABLE IV

Flow Hydrogenation of Octanoic Acid Re + Rh on Silica[a]

Cat. wt%			% Distribution					Selectivity[b]		
Re	Rh	(°C)	Hydrocarbon	Alcohol	Acid	Ester	Acid conv %	Heptane	Octane	Alcohol
4.7	–	200	0.4	1.1	82.0	14.2	10.0	1.3	2.6	83.0
4.7	–	230	2.2	0.8	80.2	14.5	11.7	14.0	4.6	70.0
4.6	2.3	200	0.8	1.6	73.8	21.9	13.8	3.8	2.2	91.6
4.6	2.3	230	6.0	12.2	39.9	38.9	38.3	11.4	4.2	83.4
4.5	4.5	200	3.8	15.3	34.0	44.1	41.2	5.5	3.8	91.5
4.5	4.5	230	30.0	28.4	13.9	22.8	73.2	29.4	11.6	54.7
2.3	4.6	200	2.4	3.3	62.5	28.8	21.2	8.3	3.0	84.0
2.3	4.6	230	12.9	13.2	38.1	31.8	44.0	23.7	5.6	66.8

[a] Conditions: pressure 300 psi, acid ≅ 18 ml/hr, H_2 ≅ 18-19 lit/hr measured at atmospheric pressure.

[b] At very high and very low concentrations, accuracy of analysis suffers significantly; hence, total does not equal 100%.

significantly large amount of hydrocarbons. The latter result from the decarboxylation (Eq. I) and the hydrogenolysis of alcohol (Eq. II) (12).

$$\text{R-COOH} \rightarrow \text{R-H} + CO_2 \quad \Delta G_f^{\circ} \tag{I}$$
$$(400K) = -19.26 \text{ Kcal/mol}$$
$$(500K) \quad -22.06 \text{ Kcal/mol}$$
$$\text{R-}CH_2OH + H_2 \rightarrow \text{R-}CH_3 + H_2O \quad \Delta_f^{\circ} \tag{II}$$
$$(400K) = -22.37 \text{ Kcal/mol}$$
$$(500K) \quad -22.40 \text{ Kcal/mol}$$

These hydrocarbons were observed in trace quantities at higher pressures; however, at lower pressures with Re_2O_7 + Ru/C, the hydrocarbons were the main or exclusive products at 230 C.

Since Ru/C synergism was not performing well at lower pressures, Pd/C promoter was examined for concentration effects. Data of this investigation are reported in Table II. As can be seen, both Re and Pd concentrations could be increased by a factor of 2, with slight sacrifice of the acid towards hydrocarbons—at 200 C and 500 psi. At 230 C pressure had to be raised since the partial pressure of steam limited the allowable partial pressure of hydrogen in the reactor. However, as is obvious, hydrocarbons now seem to be the major products.

Flow Reactor

Encouraged by the finding of synergism and applicability of the results at lower pressure, it was decided to examine the synergistic combination of elements in a flow unit. The catalysts were supported on silica gel and reduced. Liquid space velocity was ∿1—i.e., one volume of liquid was pumped through a unit volume of catalyst per hour. Effect of hydrogen space velocity was small at lower temperatures. At the higher temperature of 230 C, all tests studied gave larger amounts of hydrocarbons. Typical data for Pd + Re/SiO_2 and Rh + Re/SiO_2 at varying metal concentrations and temperature are given in Tables III and IV, respectively. At 230 C, heptane/octane ratio increased, suggesting increased interference by decarboxylation reaction.

In Figure 2, conversion of acid and selectivity to alcohols as a function of concentration of palladium on Re/SiO_2 catalyst are given. The trend is obvious in that conversions are favorably affected by higher palladium concentrations at 200 C. Selectivity is slightly lower but is within experimental error. In Figure 3, similarly, effects of Rh on Re/SiO_2 are given. Rhodium concentration affects conversions proportionally with no large effects on selectivity. The higher temperature for the same catalysts show higher conversions but selectivity is lower, such that at the highest concentration studied, ∿45% of acid charged is wasted as hydrocarbons.

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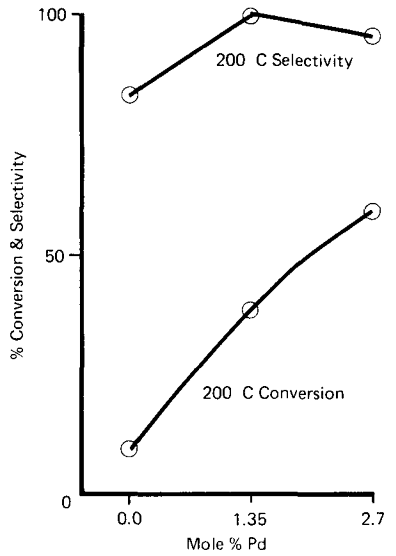

FIG. 2. Effect of Pd on Re/SiO_2.

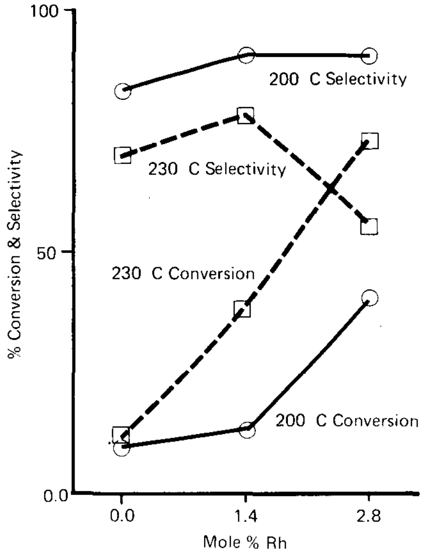

FIG. 3. Effect of Rh on Re/SiO_2.

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Fatty Acid Esters from Betulinol

V. ERÄ and **P. JÄÄSKELÄINEN**, The University of Helsinki, Department of Wood and
Polymer Chemistry, Meritullinkatu 1 A 00170 Helsinki 17, Finland, and **K. UKKONEN**,
Oy Kaukas Ab, 53200 Lappeenranta 20, Finland

ABSTRACT

Betulinol esters were prepared from stearic-, lauric-, palmitic-, oleic- and tall oil fatty acids via the acid-chloride and direct condensation routes. The degree of esterification was determined by high pressure liquid chromatography (HPLC), infrared (IR) and acid value measurements. The use of esters for air-dried, polyurethane and plastisol coatings was evaluated.

INTRODUCTION

The abundance and renewable source of the chemicals obtainable from tree bark are of increasing interest to both researchers and the chemical industry. The principal extractive component of birch bark is betulinol or betulin, which gives birch bark its white color. Betulinol is produced as a by-product in the new soap refining CSR-process (1).

Chemically, betulinol is a triterpene alcohol possessing two reactive hydroxyl groups that may be combined with fatty acids to produce esters. The work of Aslam et al. (2) indicates that betulinol can be esterified with linseed fatty acids to yield protective coating vehicles.

The object of this work was to extend knowledge on the preparation and characteristics of fatty acid esters from betulinol. Fatty acid esters were prepared from straight-chain fatty acids and betulinol via acid-chloride reaction route. Additional esters were made from some fatty acids and tall oil fatty acids using the direct condensation method. Potential use of the esters for coating applications was evaluated.

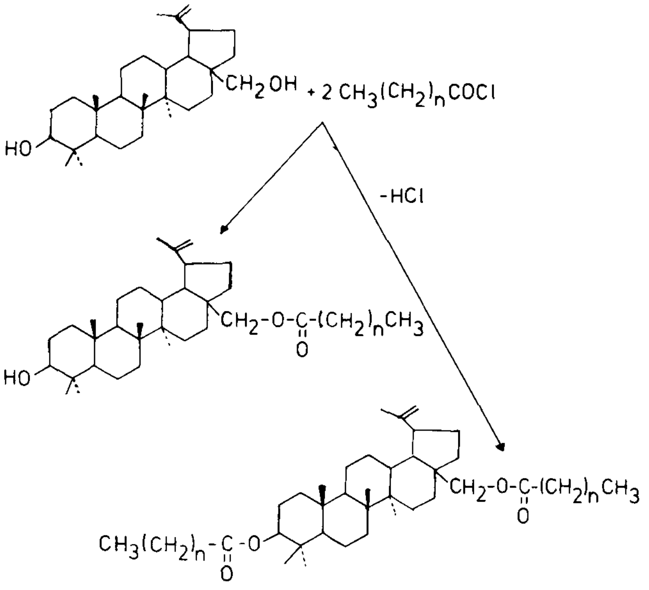
EXPERIMENTAL PROCEDURES

Betulinol was extracted from birch bark and purified by the method described elsewhere (3). The melting point of the purified betulinol was 258 C, which is in accordance with the literature values (4). The following fatty acids were used as esterifying reagents: stearic acid (mp 70 C), lauric acid (mp 44 C), palmitic acid (mp 63 C), oleic acid (mp 16 C) and a commercial fatty acid fraction of tall oil containing 95-97% fatty acids composed of 57% linoleic acids, 39% oleic acid and 4% saturated acids.

In the fatty acid chloride reaction route freshly distilled thionyl chloride (Merck p.a.) was used as a reagent. Dimethylacetamide and pyridine (Merck p.a.) were employed as solvents for betulinol.

Weighed amounts of fatty acid and excess thionyl chloride were reacted in a three necked flask equipped with a nitrogen inlet tube, a magnetic stirrer and a drying tube filled with $CaCl_2$. The mixture was heated at 80 C for 1.5 hr and unreacted thionyl chloride was removed by distillation. The amount of betulinol desired was placed in another flask and dissolved in pyridine or dimethylacetamide by bubbling nitrogen to the solution to avoid oxidation of betulinol. The formed fatty acid chlorides were added slowly to the betulinol solution. The mixture was heated at 70 C for 3 hr while bubbling nitrogen to the solution. After cooling, the reaction mixture was diluted with acetone and poured into water. The acidic water solution was extracted with ethyl ether or hexane. The separated solvent layer was

$$CH_3(CH_2)_nCOOH + SOCl_2 \longrightarrow CH_3(CH_2)_nCOCl + SO_2 + HCl$$



SCHEME I. Reaction scheme for the formation of the esters from betulinol and fatty acids via acid-chloride route.