

# Hydrogenolysis of Carboxylic Acids With Rhodium Oxide

Hydrogenolysis of a carboxylic acid or ester to the corresponding alcohol is one of the more difficult catalytic reductions. Copper chromite catalysts are relatively cheap and are commonly used, but have the disadvantage that reduction may require high temperature (6) or a large amount of catalyst (1). Carboxyl reduction is possible at lower temperatures (150 C) with ruthenium (4) or rhenium (3) oxide catalysts.

Rhodium catalysts have received very little attention for the hydrogenolysis of carboxylic acids.

groups but is said to be a poor catalyst, although no details are given (7). We have recently observed that rhodium oxide can catalyze the reduction of stearic acid to a significant degree (5) and we have now briefly explored the scope of the reaction.

As shown by Table I and Figure 1 carboxylic acids are reduced by rhodium oxide to the corresponding alcohol, then further condensed to the ester. After hydrolysis of the ester the total yield of nonyl alcohol is 49% in 6 hr, 63% in 9 hr. Esters are inert under the reaction conditions (Experiment 6) and hydrogenolysis is slower in non-polar solvents (Experiment 5).

In the reduction of benzoic acid a rapid pressure drop occurs around 75 C, corresponding to saturation of the benzene ring (2). Thus the species undergoing hydrogenolysis is really cyclohexanecarboxylic acid.

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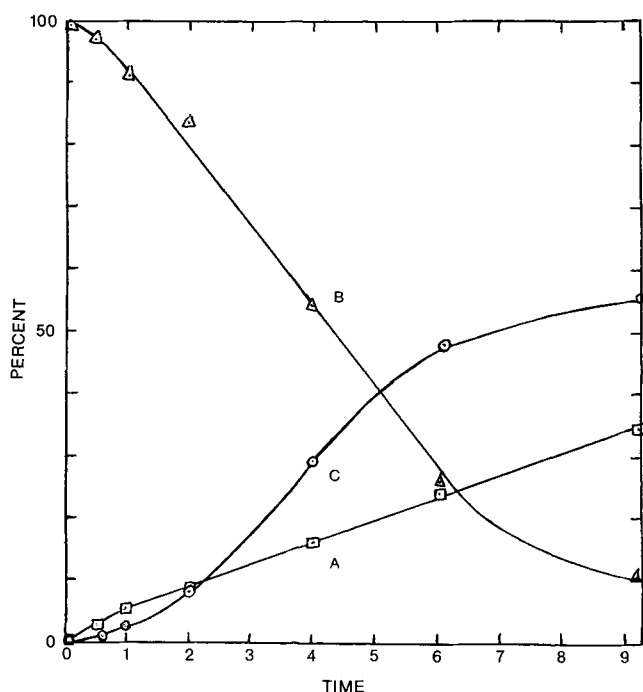


FIG. 1. Distribution of reduction products as a function of time. A, Nonanol; B, Nonanoic acid; C, Nonyl nonanoate.

TABLE I  
Carboxyl Reductions With Rhodium Oxide  
(Charge: Substrate 15 g, solvent 80 ml, Rh<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O 0.2 g. Hydrogen pressure 2000 psig.)

Experiment	Substrate	Solvent	Temperature, C	Time, hr.	Products, %
1	Nonanoic acid	Water	150	6	Nonyl alcohol 25% Nonyl nonanoate 48% Nonanoic acid 26%
2	Dodecanoic acid	Water	150	6	Dodecyl alcohol 26% Dodecyl dodecanoate 37% Dodecanoic acid 53%
3 <sup>a</sup>	Octadecanoic acid	Water	175	5	Octadecanol 10% Octadecyl octadecanoate 36% Octadecanoic acid 40%
4	Benzoic acid	Water	150	6.5	Cyclohexylmethanol 33% Cyclohexylmethyl cyclohexanecarboxylate 34% Cyclohexanecarboxylic acid 33%
5	Benzoic acid	Cyclohexane	150	3.5	Cyclohexylmethyl cyclohexanecarboxylate 15% Cyclohexanecarboxylic acid 85%
6	Methyl nonanoate	Methanol	150	5	No reaction

<sup>a</sup> Catalyst 0.1 g; hydrogen pressure 3300 psig.