BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 288 (1971)

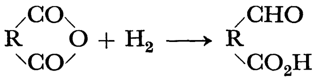
Hydrogenation of Acid Anhydrides with Cobalt Carbonyl Catalyst

Hachiro WAKAMATSU, Junko FURUKAWA, and Nobuyuki YAMAKAMI
Central Research Laboratories, Ajinomoto Co., Inc., Suzuki-cho, Kawasaki

(Received August 31, 1970)

Various carboxylic acid derivatives such as acid chlorides, imidochlorides, *N*-alkylamides, thioesters, hydrazides, and nitriles are known to give aldehydes on hydrogenation. However, little is reported[1] on the selective hydrogenation of carboxylic acid anhydrides to give aldehydes. Carboxylic acid anhydrides were found to be catalytically hydrogenated to give corresponding aldehydes and acids. Intermolecular anhydrides gave acids and aldehydes in comparable amount, whereas intramolecular anhydrides gave aldehydic acids. The new hydrogenation reaction is catalyzed by cobalt carbonyl and takes place at elevated temperatures under pressure of hydrogen and carbon monoxide. No effort was made to improve yields of the aldehydes in the experiments. The results are given in Table 1. Benzoic, acrylic, and maleic anhydrides gave anomalous results.

$$(RCO)_2O + H_2 \longrightarrow RCO_2H + RCHO$$



$$R\begin{array}{l}\diagup CO \diagdown \\ \quad\; O \\ \diagdown CO \diagup\end{array} + H_2 \longrightarrow R\begin{array}{l}\diagup CHO \\ \diagdown CO_2H\end{array}$$

The solvent effect is greater on the rate of reaction than on the hydroformylation of olefins. At 130°C, the reaction carried out in acetone gives pseudo first order rate constant five times larger than that in diethyl ether. The rate is about the same for the reaction in acetone at 130°C, that in acetic acid at 160°C, and that in benzene or cyclohexane at 175°C. When toluene was used as a solvent, the main products from acetic anhydride were reported to be acetic acid and ethyl acetate.[2] Addition of a catalytic amount of pyridine accelerates the hydrogenation reaction and thus makes the reaction possible at lower temperatures (~130°C) even in benzene and cyclohexane. Sodium iodide has an accelerating effect on the hydrogenation reaction in diethyl ether. The effect of partial pressure of carbon monoxide and hydrogen on the rate of hydrogenation of acetic anhydride is quite the same as that reported for hydroformylation and cobalt carbonyl catalyzed hydrogenation of aldehydes.[3]

TABLE 1. HYDROGENATION OF ACID ANHYDRIDES

Acid anhydride	Reaction conditions	Product
Acetic anhydride 530 mmol	$Co_2(CO)_8$ 300 mg † H_2 100, CO 100 1 hr, 20 min	Acetic acid 225 mmol Acetaldehyde 180 mmol
Propionic anhydride 230 mmol	$Co_2(CO)_8$ 300 mg † H_2 100, CO 100 2 hr, 40 min	Propionic acid 170 mmol Propionaldehyde 114 mmol
Stearic anhydride 44 mmol	$Co_2(CO)_8$ 450 mg Acetone 75 m*l* † H_2 100, CO 100 1 hr, 45 min	Stearic acid 43 mmol Stearaldehyde 25 mmol
Succinic anhydride 100 mmol	$Co_2(CO)_8$ 300 mg Dioxane 43 m*l* Pyridine 3 mmol † H_2 170, CO 30 41 hr	*β*-Formylpropionic acid 26 mmol
Glutaric anhydride 100 mmol	$Co_2(CO)_8$ 300 mg Dioxane 43 m*l* Pyridine 3 mmol † H_2 170, CO 30 4 hr, 30 min	*γ*-Formylbutyric acid 32 mmol

Reaction temperature, 130°C
A 100 m*l* capacity autoclave was used.
† Initial gas pressure in kg/cm^2, at room temperature.

When hydrogen cobalt tetracarbonyl was dissolved in acetic anhydride at −40°C and brought to −15°C, acetic acid, acetaldehyde and dicobalt octacarbonyl were obtained.

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[1] H. Musso and K. Figge, *Chem. Ber.*, **95**, 1844 (1962).

[2] I. Wender, S. Friedman, W. A. Steiner, and R. B. Anderson, *Chem. Ind.* (London), **1958**, 1694.

[3] L. Marko, *Proc. Chem. Soc.*, **1962**, 67.