Organic Syntheses by Means of Noble Metal Compounds. XIX. The Hydroformylation Reaction Catalyzed by Metallic Palladium.[1]

By Jiro Tsuji, Nobuo Iwamoto and Masanobu Morikawa

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It is known that the syntheses of aldehydes from olefins, carbon monoxide and hydrogen (Oxo reaction) are catalyzed by cobalt carbonyl. In addition, some other metal carbonyls, such as rhodium and ruthenium carbonyls, are known to be active in the reaction.

In the course of our studies of the catalytic action of metallic palladium on the carbonylation of various olefins thus, forming saturated and unsaturated carboxylic esters,[2,3] we have found that palladium chloride or metallic palladium is also active in the hydroformylation of olefins.

A typical example will be described below. In order to avoid the effect of the metal surface of an autoclave, the reaction was carried out in a glass vessel equipped with a gas-inlet capillary. Benzene (15 ml.), toluene (for the gas chromatographic determination, 2 ml.) and palladium chloride (2 g.) were mixed in the glass vessel, which was then placed in a 100-ml. autoclave. Ethylene and synthesis gas were introduced (50 and 100 kg./cm^2 respectively), and the autoclave was shaken at 100°C for 15 hr.; a 55 kg./cm^2 pressure drop was observed during this period. The amount of propionaldehyde formed was gas chromatographically determined to be 1.2 g. The conversion was not very high in general. It was confirmed that a considerable amount of ethylene was consumed by hydrogenation, thus forming ethane. Such a metallic palladium as palladium black was equally active; it seems likely, therefore, that metallic palladium is the true catalyst. The recovered palladium could be used repeatedly. The reaction procedure is simple, because metallic palladium can be used and then recovered quantitatively. The application of the method to other olefins and the reaction mechanism will be reported in a forthcoming paper.

Basic Research Laboratories
Toyo Rayon Company, Ltd.
Kamakura

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3) J. Tsuji, J. Kiji, S. Imamura and M. Morikawa, *J. Am. Chem. Soc.*, **86**, 4350 (1964).