

## A NEW CATALYTIC PATHWAY FOR METHANOL SYNTHESIS

J. W. Rathke and R. J. Klingler

Chemical Technology Division  
Argonne National Laboratory

Research Scope and Objectives. This research is devoted to the elucidation of the reaction pathways whereby homogeneous organometallic catalysts (and their heterogeneous analogs) activate small molecules, e.g., CO, and direct their subsequent reactions to specific chemical products. Intimate details connecting the molecular structures of the catalysts, the nature of intermediate species, and the thermochemical parameters of each reaction step are sought by a combination of techniques, including chemical kinetics, and spectral and isotopic studies under high-temperature and high-pressure conditions. The reactions (novel or well-known) that are being investigated often have potential significance for industrial processes of fuel conversion, energy storage, or feedstock manufacture.

Description of Research Effort. Current efforts in the area of catalytic carbon monoxide hydrogenation are based on a new concept and observation. We have found an intriguing catalyst system for the catalytic disproportionation of formate ion to form methanol as follows:



This reaction occurs at modest temperatures in molten salt solution. The following reaction has also been observed at low CO pressures:



Reaction 1 plus two times reaction 2 gives a catalytic sequence to form methanol from water and carbon monoxide:



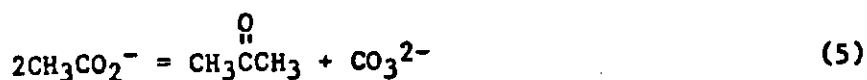
This stoichiometry, making use of H<sub>2</sub>O rather than H<sub>2</sub> as the hydrogen source, is highly desirable in terms of raw material costs. Further, this reaction is thermodynamically more favorable than the commercially used reaction involving H<sub>2</sub>:



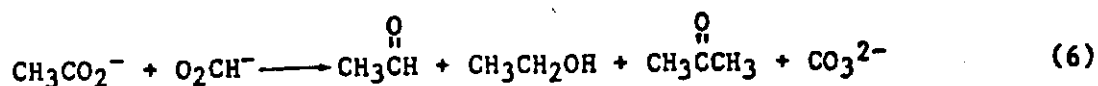
Because of the more favorable thermodynamics, higher single-pass conversions are possible with reaction 3. Note that the new catalytic CO + H<sub>2</sub>O reaction does not make use of water-gas shifting and is not a simple indirect CO + H<sub>2</sub> reaction.

As may be expected, several modifications of the catalyst have been found to be active for the system; however, the products are not always limited to methanol. In some cases, ethanol, acetone, and other organic materials are obtained. Indeed, the method has considerable practical potential for ethanol synthesis, and this possibility is currently being explored.

Reaction 1 belongs to a broader class of catalytic ketonic decarboxylation reactions which are also being studied. Additional examples of this type of reaction, for which the new catalysts show activity, are



and



At present, it seems reasonable to suspect that these reactions may account for the acetone and ethanol observed as by-products when reaction 3 is performed. However, the pathway for acetate ion formation, assuming reactions 5 and 6 are operative, remains to be determined.

Future Research. The mechanisms for the new reactions are being explored by isolation or spectroscopic observation of the catalytic intermediates and by kinetic methods. The relevance of the new chemistry to the mechanism of the commercial methanol synthesis method is also being investigated.