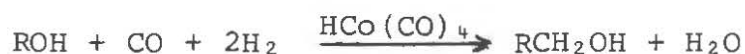# Selective Homogeneous Catalytic Methanol Homologation

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The homologation of alcohols was first reported by Wender [1] in 1949. Using the homogeneous catalyst $HCo(CO)_4$ at 180°C and 200 atm of synthesis gas, alcohols are homologated with the production of water as the by-product.

$$ROH + CO + 2H_2 \xrightarrow{HCo(CO)_4} RCH_2OH + H_2O$$

However, this reaction is intrinsically non-selective. Higher alcohols their formate and acetate esters, glycols and acetals are produced in varying quantities depending on the reaction conditions. The reason for the lack of selectivity in the cobalt catalyzed alcohol homologation process lies in the reaction mechanism [2]. Nevertheless, there has been much effort expended to increase the selectivity of this reaction for the purpose of commercialization.

In 1979, at Argonne National Laboratory, the discovery of the catalytic homologation of methanol by $Fe(CO)_5$ in the presence of a tertiary amine has opened up a new approach to this process [3].

$$CH_3OH + 2CO + H_2 \xrightarrow{Fe(CO)_5/NR_3} CH_3CH_2OH + CO_2$$
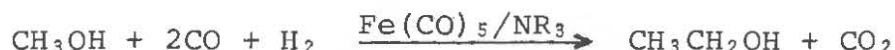
It is significant to note that ethanol is not homologated to propanol under reaction conditions and that CO_2 (as opposed to H_2O) is the oxygenated by-product. Methane production amounts to 20-60 mole percent of the converted methanol, depending on the reaction conditions.
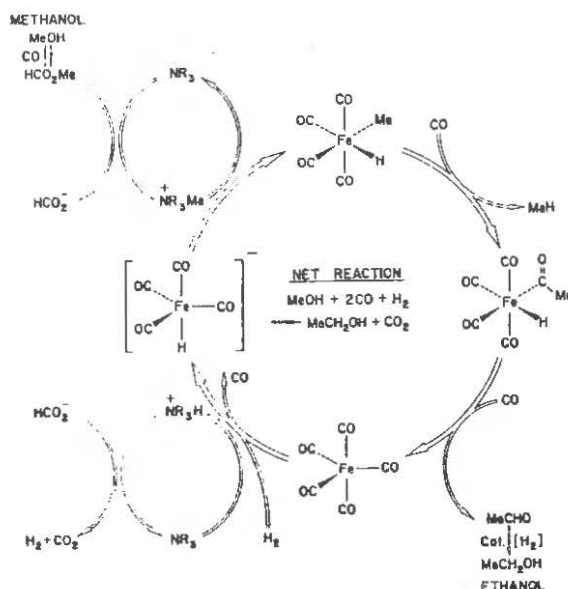
The stoichiometric methyl transfer reaction from a methyl quaternary ammonium cation to metal carbonyl anions was investigated as a

model for the rate-determining step in the homogeneous catalytic homologation of methanol[4]. The second-order nucleophilic substitution reaction was demonstrated to be first-order in both [MeNR$_3^+$] and [HFe(CO)$_4^-$] and zero-order in P_{CO} and P_{H_2}. In the temperature range of 180 - 210°C using N-methyl pyrrolidinone as a solvent, thermodynamic activation parameters were determined [$\Delta H^{\ddagger}$ = 44.1 kcal/mol, $\Delta S^{\ddagger}$ = +16.6 eu]. The rate of the methyl transfer reaction was observed to increase with decreasing dielectric constant and with decreasing salt concentration.

In the reaction of MeNR$_3^+$ with Mn(CO)$_5^-$ the product selectivity to ethanol and methane was independent of P_{CO} and P_{H_2} but was dependent on the Mn(CO)$_5^-$ concentration. At 200°C and 3600 psig of 3:1 CO/H$_2$ the difference in second-order rate constants (1.99 x 10^{-4}M^{-1}s^{-1} for HFe(CO)$_4^-$ and 5.31 x 10^{-4}M^{-1}s^{-1} for Mn(CO)$_5^-$) is an indication of the relative nucleophilicity of the metal carbonyl anions. The difference in product selectivity between the two metal systems is attributed to the presence of an intra-molecular reductive elimination mechanism competing with CO insertion for RHFe(CO)$_4$, while for RMn(CO)$_5$, an intermolecular reduction mechanism competing less effectively with CO insertion is required, and the resulting ethanol selectivity is correspondingly increased.

References

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