



Low Temperature Homologation of Ethanol Catalyzed by Ru—EDTA—CO Complex

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(Received June 13, 1988; accepted October 14, 1988)

The carbonylation of ethanol to propionic acid was catalyzed by a soluble Ru^{II}—EDTA—CO complex at 35 atm CO and at 80 °C.

Synthesis of carboxylic acids under milder conditions has been of great interest in recent years [1 - 3]. Novel homogeneous catalytic systems have been described for the carbonylation of methanol to acetic acid [1 - 3]. This reaction uses rhodium or iridium salt in the presence of a halogen promoter, *e.g.* CH₃I or HI, in a common organic solvent which catalyzes the carbonylation of methanol at 175 °C and a total pressure of 27 atm CO. The selectivity to acetic acid is 99%; significant rates of carbonylation have been observed even at atmospheric pressure. The mechanism proposed by Roth *et al.* [4] has indicated that the rate-controlling step in the carbonylation of methanol is the oxidative addition of CH₃I to the Rh(I) complex used as a catalyst in the reaction.

In the last decade many reports on the carbonylation of methanol and its homologues using different complexes of rhodium, iridium and ruthenium have appeared in the literature [5 - 7]. The basic philosophy behind all these studies is the same as that presented by Roth *et al.* [4]. Thus far it has not been possible to replace the halogen promoters and the very high temperature (175 °C) required to bring about the carbonylation of alcohols to the corresponding carboxylic acids.

Here in our laboratory we have identified the complex Ru^{II}—EDTA—CO which, in water or mixed solvent systems, can catalyze the carbonylation of benzyl chloride to phenyl acetic acid [8], carbonylation of amines to give their corresponding CO insertion products, *N*-formyl derivatives, [9] and hydroformylation of allyl alcohol to γ -hydroxybutyraldehyde [10] under much milder reaction conditions than reported in literature for the above reactions. In this paper we report the milder reaction conditions for conversion of ethanol to propionic acid at 80 °C and 34 atm CO. Though the yield

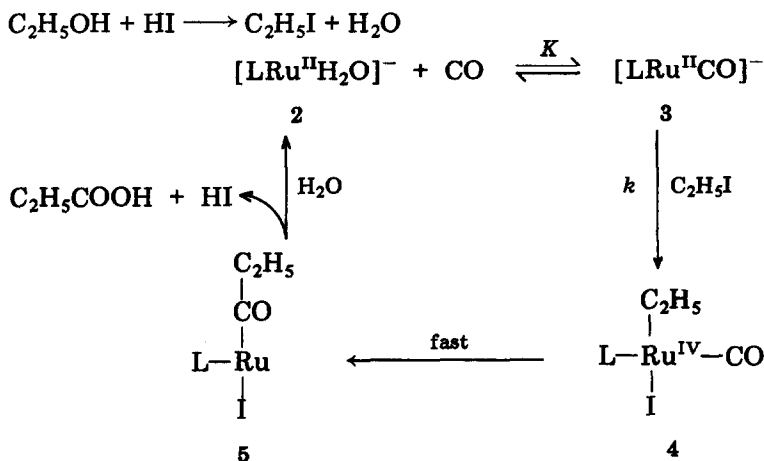
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of the carboxylated products is not high, the reaction nevertheless indicates the potential use of ruthenium complexes as catalysts in homologation at milder conditions.

The carbonylation experiments were performed in a 300 ml pressure reactor (Parr Instrument Co., USA) using pure carbon monoxide gas (99.6% purity procured from B.O.C., U.K.). In a sample run, 100 ml aqueous solution containing $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}] \cdot 2\text{H}_2\text{O}$ 1 (2 mmol), ethanol (0.34 mol) and HI (0.08 mol) was reacted at CO pressure 34 atm and 80 °C. The initial reaction mixture and other samples withdrawn at specified time intervals were analyzed for homologation products. The conversion of ethanol after a contact time of 6 h was found to be 10%, based on total ethanol concentration. The products analyzed (vol.% are given) by GLC using a 10% Carbowax column were confirmed as propionic acid (60%), ethyl propionate (30%) and diethyl ether (10%) along with unconverted ethyl iodide formed by the reaction of HI with ethanol. The overall turnover rate for ethanol conversion was found to be 2.8 mol ethanol reacted per mol catalyst per hour.

Although the turnover rate is low, the system seems to be attractive for large scale operations as there is a 50% savings in thermal energy.

The mechanism for the $\text{Ru}^{\text{II}}-\text{EDTA}-\text{CO}$ complex-catalyzed homologation of ethanol to propionic acid using CO, shown in Scheme 1, is the same as at proposed for Rh(I) and Ir(I) catalysis [4]:



Scheme 1.

In the above mechanism, ethyl iodide is formed independently in a fast reaction step. The active intermediate catalytic species 2 is formed in a faster hydrolysis of $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}] \cdot 2\text{H}_2\text{O}$ [11]. The first step is the formation of carbonyl complex 3 by the displacement of H_2O . The carbonyl complex 3 undergoes oxidative addition by $\text{C}_2\text{H}_5\text{I}$ to form an alkyl intermediate complex 4; this is the rate-determining step of the homologation reaction. Insertion of CO in the Ru-C bond of 4 forms an acyl intermediate 5, which

upon rapid hydrolysis gives propionic acid and HI, regenerating the species 2. The other products, diethyl ether and ethyl propionate, are formed by self-condensation reactions between propionic acid and ethanol.

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