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Preliminary communication

HYDROFORMYLATION OF FORMALDEHYDE

JEROME A. ROTH and MILTON ORCHIN*

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221 (U.S.A.)

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Summary

The reaction between hydridotetracarbonylcobalt and monomeric formaldehyde at 0°C in the presence of 1 atm of carbon monoxide leads to stoichiometric hydroformylation with the formation of glycolaldehyde in high yield.

Although there are patent reports [1] on the rhodium- and cobalt-catalyzed glycolaldehyde synthesis from paraformaldehyde at elevated temperatures and pressures, we wish to report what we believe is the first successful stoichiometric hydroformylation of monomeric formaldehyde. The reaction proceeds smoothly at 0°C and 1 atm of CO in excellent yield:

$$CH_2O + HCo(CO)_4 \xrightarrow[0°C,\ CH_2Cl_2]{CO,\ 1\ atm} HOCH_2CHO$$

$HCo(CO)_4$ was prepared by the disproportionation of $Co_2(CO)_8$ with pyridine, followed by acidification with H_2SO_4, according to the known procedure [2]. The gaseous $HCo(CO)_4$ was trapped in CH_2Cl_2 and the freshly prepared solution was used immediately after determining the initial concentration by titration with NaOH [3]. Usually 1.0 mmol of $HCo(CO)_4$ per 6.0 ml of CH_2Cl_2 was employed.

The mode of generating and bringing the formaldehyde monomer into contact with the $HCo(CO)_4$ solution is critical to the success of the reaction. Simply mixing the stoichiometric quantities of $HCo(CO)_4$ and CH_2O monomer usually results in rapid polymerization of the formaldehyde, even at low temperatures [4]. The preferred method consists of heating paraformaldehyde in flowing CO, and bubbling the effluent gas mixture through the $CH_2Cl_2/HCo(CO)_4$ solution at 0°C. Excess CH_2O was always used.

After the reaction the CH_2Cl_2 solution was extracted with a small amount of D_2O, the aqueous solution filtered, and the ^1H NMR spectrum recorded. The presence of glycolaldehyde was confirmed by the characteristic triplet (δ 5.3 ppm) and doublet (δ 3.8 ppm) of the hydrate. No methanol, methyl formate, or ethylene glycol was observed. The yield of glycolaldehyde was evaluated by comparison of the spectrum to that of a standardized solution and/or by adding a known amount of glycolaldehyde to the sample. Reactions performed in this way produced yields ranging from 60—90%, based on the $HCo(CO)_4$ consumed.

The relatively high yield of glycolaldehyde and the absence of methanol and methyl formate in detectable quantities indicate the strong preference of $HCo(CO)_4$ to add only in the mode which binds the cobalt to carbon rather than to oxygen.

$$HCo(CO)_4 + H_2CO \rightarrow HOCH_2Co(CO)_4 \rightarrow$$

$$HOCH_2COCo(CO)_3 \xrightarrow[CO]{HCo(CO)_4} HOCH_2CHO + Co_2(CO)_8$$

This result is of special interest in view of the controversy [5] concerning the direction of addition of $HCo(CO)_4$ to the carbonyl group of aldehydes. The stoichiometric conversions of aldehyde to alcohols has been suggested to occur via oxygen—cobalt bonding [6], while the reduction under catalytic hydroformylation conditions has been proposed to occur by carbon—cobalt bonding [7], as well as by cobalt—oxygen bonding [8,9]. The present results suggest that reaction with formaldehyde under stoichiometric conditions at low temperatures occurs essentially exclusively by carbon—cobalt bonding.

References

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