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The Effect of Methanol and Ethylene Glycol on Cobalt Carbonyl-Catalyzed Hydroformylation

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The disproportionation of $Co_2(CO)_8$ by methanol or ethylene glycol

$$3\ Co_2(CO)_8 + 12\ ROH \rightarrow 2\ Co(ROH)_6[Co(CO)_4]_2 + 8\ CO$$

is a reversible reaction the equilibrium position of which depends not only on the partial pressure of CO but also on the structure of the alcohol. Under typical catalytic hydroformylation conditions this equilibrium lies far to the left when methanol is the solvent. When ethylene glycol is added to a hydroformylation reaction, it appears to have an inhibiting effect during the early stages of the reaction because the equilibrium of Eq. (1) lies far to the right. As the reaction proceeds, however, the inhibiting effect disappears, possibly because the ethylene glycol is consumed by acetal formation.

INTRODUCTION

Investigations of the effect of solvents on the rate of hydroformylation in the presence of cobalt carbonyl catalysts show that the reaction proceeds faster in methanol (*1*) than in hydrocarbon solvents. However, it is known (*2*) that methanol, at room temperature and atmospheric pressure, rapidly disproportionates dicobalt octacarbonyl according to the equation:

$$3\ Co_2(CO)_8 + 12\ ROH \rightarrow 2\ Co(ROH)_6[Co(CO)_4]_2 + 8\ CO. \quad (1)$$

When methanol is used as a solvent under hydroformylation conditions, the question therefore arises as to the nature of the cobalt-containing catalytically active species, i.e., is Eq. (1) reversible under these conditions and, if so, to what extent? This question is also of considerable importance in connection with the conversion of methanol to ethanol (homologation) under hydroformylation conditions (*3*). Furthermore, Eq. (1) suggests that were the cationic cobalt species present under reaction conditions it might be stabilized by better coordinating ligands. In particular, will the presence of a chelating ligand alcohol such as ethylene glycol affect the position of equilibrium at the high partial pressures of carbon monoxide used in hydroformylation? The following report provides some answers to these questions.

EXPERIMENTAL

Dicobalt octacarbonyl was prepared according to the published procedure (*5*). Solvents were routinely dried over molecular sieves. Cyclohexene was purified by predrying over $CaCl_2$ and distillation from sodium under nitrogen. Pressure reactions were conducted in paired 71-ml Parr autoclaves fitted with glass liners. The reactions were conducted by mounting the auto-

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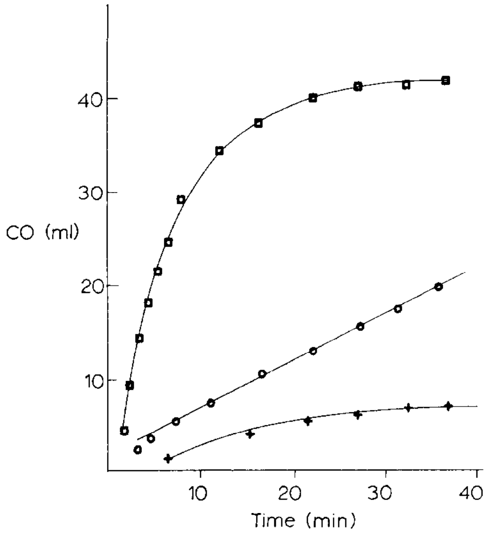

FIG. 1. Rate of CO evolution with ethylene glycol (□), methanol (○), and benzyl alcohol (+).

claves on a Burrell wrist-action shaker in an oven preheated to the appropriate temperature. Gas–liquid chromatography (glc) analyses of hydroformylation reactions were obtained on SE-30 columns operating at 100°. Determination of $Co_2(CO)_8$ was performed by measuring CO evolution on treating with excess iodine (*6*).

The reaction between $Co_2(CO)_8$ *and ethylene glycol under atmospheric pressure at 23°.* A sample of 231 mg (0.67 mmol) $Co_2(CO)_8$ was dissolved in 20 ml of dimethoxyethane in a 125-ml Erlenmeyer flask fitted with a rubber septum and connected to a gas burette. The flask was flushed with CO and then 10 ml (0.18 mol) of E. G. was injected. The reaction mixture was stirred with a magnetic stirrer and the evolved gas was collected and measured. The reaction was complete in 25 min. The results are shown in Fig. 1.

The reaction between $Co_2(CO)_8$ *and methanol under atmospheric pressure at 23°.* The same procedure as described above was repeated using 231 mg (0.67 mmol) of $Co_2(CO)_8$, 20 ml of dimethoxyethane, and 14.2 ml (0.35 mol) of methanol. After 45 min, 50% of the expected volume of gas was evolved.

The reaction between $Co_2(CO)_8$ *and benzyl alcohol under atmospheric pressure at 23°.* Starting with 231 mg (0.67 mmol) of $Co_2(CO)_8$, 20 ml of dimethoxyethane, and 36 ml (0.35 mol) of benzyl alcohol the same procedure was again employed. After 50 min, 20% of the expected volume of gas was evolved

The reaction between $Co_2(CO)_8$ *and methanol under 1400 psi at 175°.* A 71-ml autoclave containing 389 mg (1.14 mmol) of $Co_2(CO)_8$ in 10 ml of methanol was charged with 1400 psi of CO. The autoclave was shaken for 1 hr at 175°. After rapid cooling in a dry ice–acetone bath, the gas was released. The precipitate of $Co_2(CO)_8$ was separated by syringing away the supernatant liquid. The precipitate was washed with 2 ml of cold (−78°) ether followed by cold pentane. The $Co_2(CO)_8$, after drying in a stream of CO, weighed 230 mg (59%).

The reaction between $Co_2(CO)_8$ *and ethylene glycol under 1400 psi at 175°.* $[Co(C_2H_6O_2)_3][Co(CO)_4]_2$ was prepared by treating 202 mg (0.59 mmol) of $Co_2(CO_8)$ suspended in 90 ml of E.G. with 1000 psi CO at 116° for 15 hr. After slow cooling to room temperature, the gas was released and the autoclave was repressurized to 1400 psi CO. After heating and stirring for 1 hr, the autoclave was rapidly cooled to −78° and the gas was released at this temperature. The frozen reaction mixture was warmed to −8° and then extracted six times with 5-ml portions of toluene at −8°. The toluene extract was flushed with CO and was then connected to a gas burette and treated with iodine solution. The gas evolved corresponded to 2.5 mg (1.3%) of the starting $Co_2(CO)_8$.

The reaction of $Co_2(CO)_8$ *with benzyl alcohol under 1400 psi CO at 175°.* The same procedure described above for E.G. was followed, starting with 250 mg (0.73 mmol) of $Co_2(CO)_8$. The extraction step was performed with pentane at −10°. The gas evolved after treating the pentane extract with iodine solution corresponded to 150 mg (73%) of the starting $Co_2(CO)_8$.

Hydroformylation of cyclohexene in the presence of ethylene glycol (general procedure). A stock solution was prepared by mixing 9.0 ml of cyclohexene and 6.0 ml of octane. Ten milliliters of this stock solution was added to a weighed quantity of $Co_2(CO)_8$. The dark brown solution was split into two 5-ml portions and each was added to an autoclave. The appropriate quantity of E.G. was added to the reaction solution in one of the twin autoclaves. The autoclaves were sealed, flushed three times with 1000 psi of N_2 and once with 1000 psi of CO, and pressurized to 1500 psi with CO and then to 3000 psi with H_2. The autoclaves were heated for the appropriate time and cooled to 0° before venting. Results of the hydroformylation reactions are summarized in Table 1.

In the GLC analysis of the hydroformylation reaction in the presence of E.G., a new peak appeared at longer retention time than that observed for the cyclohexanecarboxaldehyde. An authentic sample of acetal was prepared from cyclohexanecarboxaldehyde and ethylene glycol; it had exactly the same retention time as the higher boiling product of the hydroformylation. A second analysis was made with a different column and again the product and authentic material had precisely the same retention time thus confirming the assignment of the unknown peak to the indicated acetal.

TABLE 1

The Effect of Ethylene Glycol on the Hydroformylation of Cyclohexene[a]

$(CH_2OH)_2$ (mmol)	Time (min)	Conversion (%)
0	60	32
3.48	60	15
0	75	53
3.48	75	49
0	105	70
3.48	105	71

[a] Reaction conditions: 150°; 3000 psi of $CO:H_2$; 0.058 mmol of $Co_2(CO)_8$ and 29.6 mmol of cyclohexene.

RESULTS AND DISCUSSION

Experiments with Methanol

When a solution of the disproportionated salt in methanol [Eq. (1)] is treated at 175° with 1400 psi of CO (initial pressure) for 1 hr, the mixture is cooled to −78°, and the pressure is released at this temperature, it is found that at least 60% of the cobalt is present at $Co_2(CO)_8$. Clearly, Eq. (1) is reversible. Accordingly, in hydroformylation reactions carried out in methanol, it is very likely that the effective catalytic species is $HCo(CO)_4$, the catalyst characteristically present in hydroformylations conducted in hydrocarbon solvents (*4*). This is also the case with the homologation reaction.

Experiments with Ethylene Glycol

The reaction of ethylene glycol (E.G.) with $Co_2(CO)_8$ at room conditions was carried out in dimethoxyethane because of the low solubility of $Co_2(CO)_8$ in E.G. The disproportionation reaction proceeded more rapidly than with methanol under the same conditions (Fig. 1).

A solution of $Co[(CH_2OH)_2]_3[Co(CO)_4]_2$ in E.G. was prepared by heating $Co_2(CO)_8$ with E.G. at 116° for 15 hr under 1000 psi of CO (initial pressure). This solution was then treated with 1400 psi of CO (initial pressure) at 175° for 1 hr. The autoclave was cooled to −78° and the pressure was released at this temperature. Analysis indicated that only 1–2% of the Co was present as $Co_2(CO)_8$. Obviously, it is more difficult to reverse Eq. (1) when E.G. is substituted for methanol.

Experiments with Benzyl Alcohol

The room temperature disproportation reaction with benzyl alcohol proceeds very slowly (Fig. 1). Under high-pressure CO at 175°, most of the cobalt (~75%) remains as $Co_2(CO)_8$ in the presence of benzyl alcohol.

Hydroformylation in the Presence of Ethylene Glycol

The rate of hydroformylation of cyclohexene in octane at 150° was determined using $Co_2(CO)_8$ as the catalyst precursor. The reaction was then repeated under similar conditions except that a 30-fold excess of E.G. over that required by the stoichiometry of Eq. (1) was added (1 mol of carbonyl to 2 mol of E.G.). These results are compared with those in which no E.G. was used (Table 1). The results show that, at relatively short reaction time and low conversion, there is a definite difference in rate with and without E.G. However, as the reaction proceeds, this difference disappears, and, after 105 min, the percentage completion is virtually the same (~70%). Analysis of the product formed at long reaction times showed considerable acetal present. Hence it is possible that, because the aldehyde formed in the reaction consumes the E.G. by such acetal formation, the gradual depletion of E.G. may be responsible for the loss of its inhibiting effect as the reaction goes to completion.

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