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IS THE HYDROFORMYLATION REACTION REVERSIBLE ? *

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Summary

Treatment of 3,3-diphenyl-1-propanol under cobalt-catalyzed hydroformylation conditions gives the corresponding aldehyde as the principal product but a small quantity of 1,1-diphenylethylene is also formed. Similarly 3-phenyl-1-propanol gives a small quantity of styrene. These arylethylenes are probably generated via the radical dehydrogenation to the corresponding aldehydes followed by decarbonylation and dehydrogenation, a reaction pathway that constitutes the reverse of the hydroformylation reaction. Attempts to rearrange isobutyraldehyde to the straight chain isomer (and the reverse) did not yield significant quantities of the rearranged product. The aldehydes obtained by cobalt-catalyzed hydroformylation apparently undergo the reverse reaction but at such a slow rate that the back reaction can usually be neglected.

Introduction

The relative rates, regiospecificity, and stereochemistry observed in the hydrogenation of various polynuclear aromatic hydrocarbons when carried out under cobalt-catalyzed hydroformylation conditions [1] have been rationalized [2] on the basis of a free radical mechanism involving hydrogen atom transfer from $HCo(CO)_4$. Hydrogen transfer reactions from donors such as 9,10-dihydroanthracene to acceptors such as 1,1-diphenylethylene at 150 °C under 100 atmospheres of CO proceed in quantitative yield. These transfer reactions have also been shown [3] to be radical in nature, initiated by $^{\cdot}Co(CO)_4$ generated by thermal dissociation of $Co_2(CO)_8$ [4].

The catalytic hydroformylation of alkenes frequently gives not only the expected aldehydes but the corresponding alcohols as well; indeed at higher temperatures (180–200 °C) the alcohols are the principal products. With the knowledge that radical reactions occur under these conditions we were curious as to whether the

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* This article is dedicated to Professor Jack Halpern whose seminal contributions to the understanding of homogeneous catalysis has served and inspired a generation of workers in this field.

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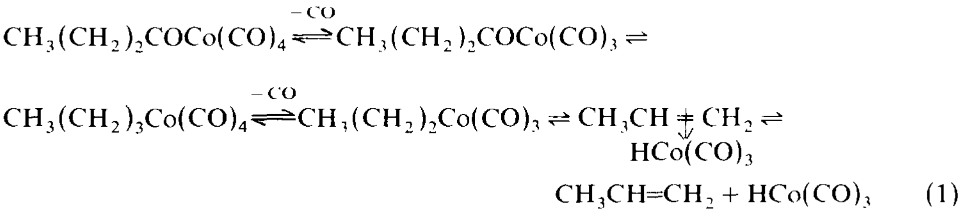
aldehyde-alcohol reaction was reversible and were led to submit 3,3-diphenyl-1-propanol to catalytic hydroformylation conditions. Not only did we observe the presence of 3,3-diphenyl-1-propanal in the product but we detected a small quantity of 1,1-diphenylethylene as well. This opened up the question as to whether the hydroformylation reaction is completely reversible, a question which to the best of our knowledge has never been explicitly addressed previously.

Results and discussion

The sequence of steps in the hydroformylation mechanism leading to intermediate acylcobalt carbonyls is known to be reversible [5]. Thus when n-butyroylcobalt tetracarbonyl prepared from $NaCo(CO)_4$ and $n\text{-}C_3H_7COCl$ is prepared under 1 atm CO it is quite stable. However, when the CO is replaced by N_2, slow isomerization to isobutyroylcobalt carbonyl occurs accompanied by a disproportionation reaction in which n- and isobutyraldehyde as well as propylene are formed. These products are readily explained by the reversal of the hydroformylation sequence, eq. 1. The



$$CH_3(CH_2)_2COCo(CO)_4 \overset{-CO}{\rightleftharpoons} CH_3(CH_2)_2COCo(CO)_3 \rightleftharpoons$$

$$CH_3(CH_2)_3Co(CO)_4 \overset{-CO}{\rightleftharpoons} CH_3(CH_2)_2Co(CO)_3 \rightleftharpoons CH_3CH \underset{\underset{HCo(CO)_3}{\downarrow}}{=} CH_2 \rightleftharpoons$$

$$CH_3CH{=}CH_2 + HCo(CO)_3 \qquad (1)$$

$HCo(CO)_3$ formed in eq. 1 can then proceed to hydroformylate propylene as well as cleave the two isomeric acylcobalt complexes and give the mixture of aldehydes observed.

It is generally assumed that the final step in the hydroformylation reaction, the cleavage of acylcobalt complexes to aldehydes, is irreversible in the stoichiometric reaction as well as in the catalytic reaction. Under catalytic conditions either $HCo(CO)_4$ or H_2 (or both) is the hydrogenolysis reagent, eq. 2.

$$RCOCo(CO)_{3,4} \xrightarrow[(H_2)]{HCo(CO)_4} RCHO + Co_2(CO)_8(HCo(CO)_{3,4}) \qquad (2)$$

Most of the published literature on the subject [6] assumes that eq. 2 is irreversible but our observation that $Ph_2C{=}CH_2$ is formed in small amounts when $Ph_2CHCH_2CH_2OH$ is treated under catalytic hydroformylation conditions suggested otherwise. Furthermore we were able to find very small quantities of $PhCH{=}CH_2$ on similar treatment of $PhCH_2CH_2CH_2OH$.

We were encouraged in the reversibility hypothesis by close examination of an early patent disclosure [7] involving product selectivity in the hydroformylation of propylene. Thus it was reported that if the hydroformylation were carried out in the presence of isobutyraldehyde, the formation of n-butyraldehyde was enhanced while in the presence of n-butyraldehyde the selectivity to branched chain isomer was increased. This control, we thought, might be exercised by the reversibility of the final step of the hydroformylation (eq. 2), followed by the known equilibria represented by eq. 1, the selectivity resulting from the mass action effect on the equilibria involved.

However all of our attempts to rearrange isobutyraldehyde or n-butyraldehyde under hydroformylation conditions failed to give significant quantities of a rearranged product. Short contact times give little conversion of the aldehydes and exposure of aldehydes to long contact times under catalytic conditions leads to formates, acetals, and other high boiling materials. We are at a loss to rationalize the patent claims.

The (equilibrium) conversion of primary alcohols (3,3-diphenyl-1-propanol; 3-phenyl-1-propanol; 1-hexanol) to aldehydes [8] under catalytic hydroformylation conditions (eq. 3) very likely proceeds by a $Co(CO)_4$ radical initiated process.

$$\mathrm{Co_2(CO)_8 \rightleftharpoons 2\ Co(CO)_4}$$

$$\mathrm{Co(CO)_4 + PhCH_2CH_2CH_2OH \rightleftharpoons PhCH_2CH_2\dot{C}HOH + HCo(CO)_4}$$

$$\mathrm{PhCH_2CH_2\dot{C}HOH + Co(CO)_4 \rightleftharpoons PhCH_2CH_2CHO + HCo(CO)_4}$$

$$\mathrm{2HCo(CO)_4 \rightleftharpoons Co_2(CO)_8 + H_2}$$

$$\mathrm{PhCH_2CH_2CH_2OH \rightleftharpoons PhCH_2CH_2CHO + H_2} \tag{3}$$

The presence of small quantities of $PhCH_2CH_3$ and $PhCH{=}CH_2$ in the above reaction suggested the possibility that once the aldehyde were formed it may undergo reverse hydroformylation to styrene which would then proceed to react in the well-known manner to give ethylbenzene and aldehydes [9]. The reaction of pure styrene under mild conditions not only gives ethylbenzene and 3-phenylpropanal but also considerable branched chain aldehyde, $PhCH(CH_3)CHO$. We could find only traces of this aldehyde. However, even under the mild conditions of the stoichiometric reaction it has been shown [10] that the branched acylcobalt complexes from styrene can rearrange to the thermodynamically more stable linear product which predominates at high temperatures [11].

The formation of ethylbenzene and styrene from 3-phenyl-1-propanol (and analogously, 1,1-diphenylethane and 1,1-diphenylethylene from 3,3-diphenyl-1-propanol) involves the intermediate formation of the 3-phenylpropanal, (eq. 3), since the aldehyde also gives these products. The aldehyde may then react according to the sequence shown in eq. 4–7.

$$\mathrm{PhCH_2CH_2CHO + {}^{\bullet}Co(CO)_4 \rightleftharpoons PhCH_2CH_2\dot{C}{=}O + HCo(CO)_4} \tag{4}$$

$$\mathrm{PhCH_2CH_2\dot{C}{=}O \xrightarrow{-CO} PhCH_2\dot{C}H_2} \tag{5}$$

$$\mathrm{PhCH_2\dot{C}H_2}\begin{cases}\xrightarrow{\mathrm{HCo(CO)_4}} \mathrm{PhCH_2CH_3 + {}^{\bullet}Co(CO)_4} & (6)\\ \qquad (\mathrm{H_2})\upharpoonleft\!\downharpoonright & \\ \xrightarrow{\mathrm{{}^{\bullet}Co(CO)_4}} \mathrm{PhCH{=}CH_2 + HCo(CO)_4} & (7)\\ \qquad\qquad\downarrow & \\ \qquad\quad \text{aldehydes (trace)} & \end{cases}$$

We have recently proposed [12] that the aldehyde-forming step of the stoichiometric hydroformylation is a radical reaction involving the abstraction of a hydrogen atom from the acyl radical generated by the homolysis of the acylcobalt carbonyl (eq. 8). Were the acyl radical formed, some decarbonylation might be expected. We

TABLE 1

EXPERIMENTS TO TEST HYDROFORMYLATION REVERSAL[a]

Reactant (mmol)	$Co_2(CO)_8$ (mmol)	Solvent (ml)	Time (h)	Yield of products[b] (%)		
$Ph_2CHCH_2CH_2OH$ (10)	1.46	C_6H_{12} (10)	20	Ph_2CHCH_3 (4.7)	$Ph_2C{=}CH_2$ (3.3)	Ph_2CHCH_2CHO (18.4)
$PhCH_2CH_2CH_2OH$ (20)	2.93	C_6H_{12} (20)	20	$PhCH_2CH_3$ (1.1)	$PhCH{=}CH_2$ (1.4)	$PhCH_2CH_2CHO$ (9.9)
$PhCH_2CH_2CHO$ (60)	8.79	C_6H_{12} (20)	20	$PhCH_2CH_3$ (8.2)	$PhCH{=}CH_2$ (0.4)	$Ph(CH_2)_2CH_2OH$ (37.8)[c]
$PhCH_2CH_3$ (200)	6.00	None	6		$PhCH{=}CH_2$ (0.2)	
$PhCH_2CH_3$ (20)	2.93	C_6H_{12} (20)	6		$PhCH{=}CH_2$ (0.2)	
$CH_3(CH_2)_4CH_2OH$ (20)	2.93	C_6H_{12} (20)	20	C_5 hydrocarbons (3.9)[d]		$CH_3(CH_2)_4CHO$ (3.1)
$CH_3CH(CH_3)CHO$ (200)	5.86	n-C_8H_{18} (100)	17		–	$CH_3CH(CH_3)CH_2OH$ (59.0)
$CH_3CH_2CH_2CH_2O$ (676) $CH_3CH_2CH_2CH_2OH$ (555) H_2O (153)	16.5	–	6	–	–	$CH_3CH_2CH_2CH_2OH$ (66.0)[e]
$CH_3CH_2CH_2CHO$ (80)	5.86	p-cymene (20)	20	$CH_3(CH_2)_3OH$ (41.5)[f]	$CH_3CH(CH_3)CH_2OH$ (0.5)	$CH_3CH(CH_3)CHO$ (1.3)

[a] At 150 °C with 1:1 H_2/CO (3000 psig initial). [b] Unless otherwise noted the percent reactant remaining is 100 minus the sum of the yield of products [c] About 47.7% of higher-boiling materials present. [d] This is a minimum value owing to losses of the volatile C_5 fraction. [e] The balance was high-boiling materials. [f] About 56.2% higher boiling material present including n-butyl formate.

$$R\dot{C}{=}O + HCo(CO)_4 \rightarrow RCHO + {}^{\cdot}Co(CO)_4 \qquad (8)$$

have treated phenylacetaldehyde with $Co_2(CO)_8$ under catalytic hydroformylation conditions and found a small quantity of toluene in the products indicating that even under high partial pressures of CO, some decarbonylation is possible. It will be noted that reaction 4 is the reverse of eq. 8. Thus it is likely that under catalytic hydroformylation conditions, the conversion of acylcobalt complexes to aldehydes is indeed reversible with the equilibrium lying far on the side of the aldehyde.

The small quantity of styrene found in the reactions of 3-phenylpropanal and 3-phenyl-1-propanol can conceivably arise from the ethylbenzene formed from these compounds. When ethylbenzene was treated under hydroformylation conditions a small quantity of styrene indeed was formed. We believe this arises by hydrogen atom abstraction of a benzylic hydrogen by $^{\cdot}Co(CO)_4$. Similar explanations can account for the presence of $Ph_2C{=}CH_2$ in the experiments with $Ph_2CHCH_2CH_2OH$.

In conclusion it appears that the aldehyde-forming step in the cobalt-catalyzed hydroformylation reaction is very likely reversible but the reverse reaction makes little contribution to the overall reaction and usually can be neglected.

Experimental

Dicobalt octacarbonyl was prepared according to the procedures in the literature [13]. All other chemicals were purchased either from Aldrich or Eastman Kodak (reagent grade) and were used without any further purification. 1-Butanol was purchased from Fisher and was purified by distillation.

Reactions were usually carried out in a 70 ml shaking autoclave with a glass liner. A 150 ml stirring autoclave was used for the C_4 aldehyde reactions.

Reaction products were analyzed by GLC using a 2% OV-17/Chromosorb W column (1/4 in ×6 ft; 60 ml/min helium) at the following temperatures; 165 °C isothermal for 3,3-diphenyl-1-propanol, temperature programmed 90–120 °C for 3-phenyl-1-propanol, and 70–200 °C for 3-phenylpropanal. The other reaction products were analyzed using a 15% SE-30/Chromosorb W column (1/4 in.× 20 ft; 60 ml/min helium) at the following temperatures; 70 °C isothermal for C_4 aldehydes and 1-hexanol and 85 °C for ethylbenzene. The results are summarized in Table 1. Treatment of $PhCH_2CHO$ (20 mmol) with $Co_2(CO)_8$ (2.93 mmol) in 20 ml cyclohexane at 150 °C with 3000 psi 1 : 1 H_2/CO for 20 h gave 1.0% toluene, 31.1% $PhCH_2CH_2OH$, 3.5% recovered aldehyde, and 64.4% of the type of high boiling material characteristic of exposing aldehydes to such conditions for long periods. The analysis was done by GLC using 15% SE-30 with temperature programming from 80–200 °C.

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