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BEHAVIOUR OF ACYLCOBALT CARBONYLS UNDER "OXO" CONDITIONS

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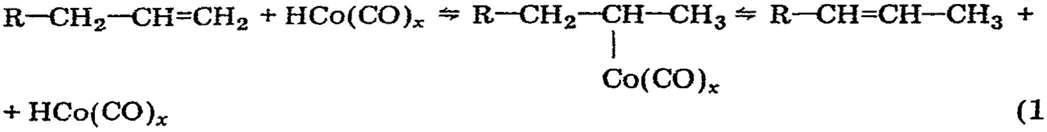
The behaviour of acylcobalt carbonyls under a variety of conditions has been investigated in recent years because of the eventual importance of these compounds in determining the isomeric distribution of the aldehydes formed by the hydroformylation of olefins catalysed by cobalt derivatives. Acylcobalt carbonyls have in fact been detected during the hydroformylation of olefins in the reaction medium [1, 2] and have been assigned a relevant role in the reaction mechanism by Heck [3].

Takegami et al. [4—9] have studied the behaviour of acylcobalt carbonyls in various solvents at temperatures between 0 and 30°C in an atmosphere of CO or N_2. An extensive isomerization has been noticed depending on solvents, temperature and atmosphere. As a consequence of these results isomerization of acylcobalt carbonyls has been suggested as the reaction step responsible for isomer formation in the hydroformylation of olefins. More recently Rupilius and Orchin [10], through a very careful investigation carried out at atmospheric pressure, have been able to show that acylcobalt carbonyls, at room temperature and under nitrogen, disproportionate into olefin and aldehyde. These reactions if taking place under "oxo" conditions could cause the formation of isomeric aldehydes.

In the present work we have been trying to find out if these two reactions, the isomerization and the disproportionation of acyl cobalt carbonyls, could take place under "oxo" conditions, that is at temperatures above 80°C and CO and H_2 pressure exceeding 50 atm. A number of data reported in the literature are in fact in disagreement with the suggested isomerization of intermediate acylcobalt carbonyls during the hydroformylation reaction of olefins and demand further investigation of the field.

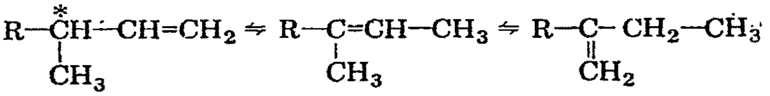
The absence of any significant amount of isomerized olefin in the reaction medium during the hydroformylation of pentene-1 at a CO pressure exceeding 90 atm. [11], and the constant nature of the isomeric composition of the products throughout the whole reaction does not seem to support the isomerization of acyl- and alkylcobalt carbonyls during the reaction as suggested by Heck [3] and Takegami [4]. Such isomerization was supposed to take place through the decomposition of alkylcobalt carbonyls into a cobalt carbonyl hydride and olefin.

More evidence against the isomerization of the olefin through alkylcobalt carbonyl formation and decomposition (1)



$$\mathrm{R{-}CH_2{-}CH{=}CH_2 + HCo(CO)_x \rightleftharpoons R{-}CH_2{-}\underset{\displaystyle Co(CO)_x}{\underset{|}{CH}}{-}CH_3 \rightleftharpoons R{-}CH{=}CH{-}CH_3 + HCo(CO)_x} \qquad (1)$$

is provided by the results of the hydroformylation of optically active olefins [12-14]. The high optical yield with which optically active aldehydes have been obtained is a proof that no isomerized free olefin, where the double bond binds to the originally asymmetric carbon atom, may be an intermediate of this reaction (2).



$$\mathrm{R{-}\overset{*}{\underset{\displaystyle CH_3}{\underset{|}{C}}}H{-}CH{=}CH_2 \rightleftharpoons R{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_3 \rightleftharpoons R{-}\underset{\displaystyle CH_2}{\underset{\|}{C}}{-}CH_2{-}CH_3} \qquad (2)$$

The formation of only one aldehyde by carbonylation of orthoformic esters [15, 16] (3) in the presence of cobalt catalysts which proceeds, under

$$\mathrm{HC(O{-}}n\mathrm{C_3H_7)_3 + CO + H_2 \rightleftharpoons CH_3{-}CH_2{-}CH_2{-}CHO + HCOOC_3H_7 + CH_3{-}CH_2{-}CH_2OH} \qquad (3)$$

conditions identical to those of the hydroformylation, through alkyl- and acylcobalt carbonyls [17] provides further evidence that these intermediates under "oxo" conditions do not significantly contribute to the formation of isomeric aldehydes.

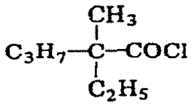
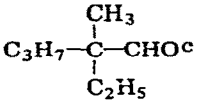
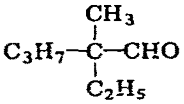
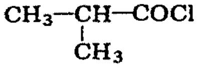
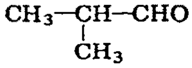
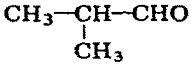
In order to provide more direct evidence on the irrelevance of the contribution, if any, of the isomerization of acylcobalt carbonyls to the formation of isomeric aldehydes we have investigated the behaviour of some representative acylcobalt carbonyls under a pressure of CO and H_2 of at least 80 atm. and a temperature of 80°C. Acylcobalt carbonyls were prepared by mixing, in an autoclave, a solution of $NaCo(CO)_4$ in ethyl ether with a solution of an acylchloride in the same solvent at -80°C under CO (80 atm.). The reactor was then placed in ice and rocked for 8 h.

A first series of experiments was run, heating the autoclave at 80°C for 5 h under CO at 80 atm. The autoclave was then cooled to -80°C and a sample of the solution was collected and analyzed by GLC. In the second series of experiments, after heating the reactor at 80°C for 10 min, hydrogen was added (80 atm.) and after 5 h the product was collected and analyzed as before. The results obtained are reported in Table 1.

It is evident that under the rather high pressure of carbon monoxide, acylcobalt carbonyls even at 80°C are relatively stable: after 5 h only a fairly low conversion to aldehydes and olefins was detected accompanied by a very small formation of isomeric aldehydes. In the presence of hydrogen neither

TABLE 1

Experimental results ($NaCo(CO)_4$, 0.016 mole; acyl chloride, 0.014 mole; diethyl ether, 60 ml; p_{CO}, 80 atm.; T, 80°C; 5 h.).

Acyl compound	p_{H_2} (atm)	Conversion to aldehyde[a] (%)	Aldehyde formed	Yield[b] (%)	Olefin
 $C_3H_7-C(CH_3)(C_2H_5)-COCl$	—	15	 $C_3H_7-C(CH_3)(C_2H_5)-CHO$[c]	92	Hexenes
			Other C_7 aldehydes[c]	8	
	80	35	 $C_3H_7-C(CH_3)(C_2H_5)-CHO$	100	Absent
 $CH_3-CH(CH_3)-COCl$	—	30	 $CH_3-CH(CH_3)-CHO$	95	Propene
			$CH_3-CH_2-CH_2-CHO$	5	
	80	62	 $CH_3-CH(CH_3)-CHO$	100	Absent
$CH_3-CH_2-CH_2-CH_2-COCl$	—	n.d.	$CH_3-CH_2-CH_2-CH_2-CHO$	98	Butenes
			Other C_5 aldehydes	2	
	80	n.d.	$CH_3-CH_2-CH_2-CH_2-CHO$	100	Absent

[a] Moles total aldehydes/moles acyl chloride.
[b] Moles aldehyde/moles total aldehydes.
[c] Identified as methyl ester of corresponding acid.

dismutation nor isomerization reactions take place but only reduction to the expected aldehydes. Under "oxo" conditions therefore, acylcobalt carbonyls do not isomerize to any significant extent and therefore this reaction cannot be considered responsible for the formation of isomeric aldehydes in the hydroformylation of olefins.

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