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HYDROFORMYLATION OF DEUTERATED OLEFINS IN THE PRESENCE OF COBALT CATALYSTS

II *. EXPERIMENTS AT LOW PRESSURE OF CARBON MONOXIDE **

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Summary

Complete retention of deuterium is observed during the hydroformylation of deuterated olefins even with a low partial pressure of carbon monoxide. Inter- and intra-molecular redistribution of deuterium does take place, however. An olefin—catalyst complex containing two molecules of olefin is suggested to rationalize the results.

Introduction

The partial pressure of the carbon monoxide has a significant influence on the course of the hydroformylation of olefins in the presence of cobalt catalysts [1,2]. With a relatively high partial pressure of carbon monoxide a higher percentage of the least branched product is formed and no olefin isomerization is detected, but with a low carbon monoxide pressure the percentage of the more branched isomers is increased and the residual olefin is siomerized, to an extent which is higher the lower the pressure of carbon monoxide used.

In order to study this effect we have extended to low carbon monoxide partial pressures our investigation of the hydroformylation of deuterated olefins under relatively high carbon monoxide partial pressures [3]. We wanted to find out if

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* Part I see ref. 3.

** Preliminary results: ref. 6a, b.

TABLE 1

HYDROGEN DISTRIBUTION ON THE CARBON ATOMS OF THE STRAIGHT-CHAIN ESTERS DERIVED FROM THE HYDROFORMYLATION PRODUCTS FROM VARIOUS OLEFINS (olefin 2 g; $Co_2(CO)_8$ 0.25 g; solvent 25 ml; $p(H_2)$ 80 atm; T 100°C)

Olefin	p(CO) (atm)	Number of hydrogen atoms on carbon atoms					
		2	3	4	5	6	7
$CD_3CH{=}CH_2$	1.5	1.13	1.08	1.78			
	S.D. [a]	1.148	1.148	1.714			
$CD_3CH_2CH{=}CH_2$	1.5	1.32	1.29	1.42	1.97		
	S.D. [a]	1.33	1.33	1.33	2.00		
$CD_3(CH_2)_2CH{=}CH_2$	5.0	1.53	1.55	1.82	1.82	1.28	
	1.5	1.40	1.43	1.50	1.60	2.07	
	S.D. [a]	1.455	1.455	1.455	1.455	2.180	
$CD_3(CH_2)_3CH{=}CH_2$	1.5	1.55	1.48	1.66	3.17		2.14
	S.D. [a]	1.538	1.538	1.538	1.538	1.538	2.308

[a] S.D.: statistical distribution.

under these new conditions there was deuterium retention and inter- and/or intra-molecular redistribution.

Results

The experimental technique was that described previously [3]. The results are reported in Table 1.

The data show that even under a low partial pressure of carbon monoxide there is no loss of deuterium from the substrate, and thus the reaction must proceed by a mechanism which does not allow incorporation of gaseous hydro-

TABLE 2

MASS SPECTRA (20 eV) OF THE METHYL ESTERS DERIVED FROM THE HYDROFORMYLATION PRODUCTS OF DEUTERATED OLEFINS AT 1.5 atm p(CO)

Ester	Relative intensity of peaks			m/e
	M	$M+1$	$M+2$	
Methyl butyrate deuterated	100	79.3	51.9	105
non deuterated [a]	100	38.0		102
calculated	100	5.6	0.5	102
Methyl pentanoate deuterated	100	47.6	4.3	119
non deuterated [a]	100	7.1		116
calculated	100	6.7	0.6	116
Methyl hexanoate deuterated	100	44.0	6.0	133
deuterated [b]	100	30.0	4.0	133
non deuterated [a]	100	8.3		130
calculated	100	7.9	0.7	130
Methyl heptanoate deuterated	100	34.0	4.4	147
non deuterated [a]	100	11.1	1.3	144
calculated	100	9.0	0.8	144

[a] Spectra obtained with non-deuterated reference products. [b] Experiment at 5 atm p(CO).

gen in the substrate apart from that introduced in the hydroformylation reagent itself.

The distribution of deuterium in the products obtained from hydroformylation experiments at very low carbon monoxide pressures is almost statistical. In the products obtained from the hydroformylation of pent-1-ene-5-d_3 under 5 atm carbon monoxide the distribution of deuterium is somewhere between that observed with 80 atm p(CO) [3] and that with 1.5 atm p(CO).

Of special significance is the fact that, with a relatively high partial pressure of carbon monoxide, deuterium was absent in position 4 of the straight-chain product deriving from but-1-ene-4-d_3, in position 4 and 5 of the product from pent-1-ene-5-d_3 and in position 4, 5 and 6 of the product from hex-1-ene-6-d_3, whereas in the same products obtained with a very low p(CO) deuterium is present on all the carbon atoms.

Intermolecular transfer of deuterium and hydrogen increases as shown by the mass spectra of the products (Table 2), as the pressure of carbon monoxide is decreased.

Discussion

The total retention of deuterium accompanied by its redistribution, which under a very low pressure of carbon monoxide approaches a statistical distribution, is an indication of an olefin isomerization mechanism which does not involve release of free cobaltcarbonyl hydride [3]. Under these conditions residual olefin is strongly isomerized, and deuterium is completely retained but is spread over all the carbon atoms of its chain. This isomerization can be explained by postulating that the transfer of deuterium occurs through an intermediate olefin—catalyst complex containing two molecules of olefin. The intermolecular transfer of deuterium may also involve this complex.

Alkylcobalt carbonyls decompose and isomerize when working under conditions analogous to those described in this paper (low p(CO)) [4]. Therefore we cannot exclude that olefin isomerization and deuterium redistribution, under these conditions, are at least in part due to a mechanism involving alkylcobalt carbonyl formation and decomposition, but we must emphasize the fact that such formation and decomposition of alkylcobalt carbonyl would have to take place without release of free cobaltcarbonyl hydride, since if this were the case we should detect a loss of deuterium in the reaction products and in the isomerized olefin.

Experimental

GLC analyses were performed on a Perkin—Elmer model F 30 instrument. Isomeric esters were separated with a Perkin—Elmer GLC F 21 preparative instrument.

NMR spectra were recorded on a Varian T 60 and on a Perkin—Elmer R 32 spectrometers. Mass spectra were recorded on a Perkin—Elmer model 270 B mass spectrometer.

The determinations of the amounts of hydrogen on the various carbon atoms of the hydroformylation products involved integration of the NMR spectra of solutions of the corresponding methyl esters in C_6D_6 using $Eu(DPM)_3$ as shift reagent. The methyl group of the $-COOCH_3$ moiety served as internal standard.

Materials

But-1-ene-4-d_3, pent-1-ene-5-d_3 and hex-1-ene-6-d_3 were prepared as previously described [3].

Propene-3-d_3. Propionic acid-3-d_3 (29 g), obtained in 75% yield via a malonic synthesis starting with CD_3Br [3], was treated at 0°C with $LiAlH_4$ (15.3 g) in diethyl ether (300 ml). The mixture was refluxed for 6 h, treated with acetic anhydride and subsequently distilled to yield propyl-3-d_3 acetate (23 g), b.p. 101°C, n_D^{20} 1.2842, NMR (int. TMS): δ (ppm) 1.80 (m, 2.00 H, $CD_3\underline{CH_2}CH_2$), 2.10 (s, 3.00 H, $\underline{CH_3}COO$), 4.12 (t, 2.00 H, $CD_3CH_2\underline{CH_2}$). On pyrolysis at 480°C this gave propene-3-d_3 (5.2 g). The NMR of its dibromo derivative showed (int. TMS, solvent CCl_4): δ (ppm) 3.65 (m, 2.00 H, $CHBr\underline{CH_2}Br$), 4.15 (m, 1.00 H, $\underline{CH}BrCH_2Br$).

Hydroformylation of olefins and identification of products

Olefins were hydroformylated as described previously [5]. Conditions used are shown in Table 1. For propene-3-d_3 and but-1-ene-4-d_3, toluene was used as solvent. In the other cases benzene was used.

Aldehydes were converted into the methyl esters of the corresponding carboxylic acids in the usual manner [5]. The esters were analyzed and separated by GLC.

NMR spectra of the esters from experiments at 1.5 atm p(CO):

Methyl butyrate (int. TMS, solvent C_6D_6, $Eu(DPM)_3$): δ (ppm) 1.43 (m, 1.78 H, $\underline{CH_3}CH_2$), 2.92 (m, 1.08 H, $CH_3\underline{CH_2}$), 4.10 (m, 1.13 H, $\underline{CH_2}COOCH_3$), 5.30 (s, 3.00 H, $COO\underline{CH_3}$).

Methyl pentanoate (int. TMS, solvent C_6D_6, $Eu(DPM)_3$): δ (ppm) 1.11 (m, 1.97 H, $\underline{CH_3}CH_2$), 2.48 (m, 1.42 H, $CH_3\underline{CH_2}$), 4.15 (m, 1.29 H, $CH_3CH_2\underline{CH_2}$), 5.94 (m, 1.32 H, $\underline{CH_2}COOCH_3$), 7.06 (s, 3.00 H, $COO\underline{CH_3}$).

Methyl hexanoate (int. TMS, solvent C_6D_6, $Eu(DPM)_3$): δ (ppm) 1.05 (m, 2.07 H, $\underline{CH_3}CH_2$), 1.71 (m, 1.60 H, $CH_3\underline{CH_2}$), 2.49 (m, 1.50 H, $CH_3CH_2\underline{CH_2}$), 4.18 (m, 1.43 H, $\underline{CH_2}CH_2COOCH_3$), 5.94 (m, 1.40 H, $\underline{CH_2}COOCH_3$), 7.04 (s, 3.00 H, $COO\underline{CH_3}$).

Methyl heptanoate (int. TMS, solvent C_6D_6, $Eu(DPM)_3$): δ (ppm) 0.96 (t, 2.14 H, $\underline{CH_3}CH_2$), 1.65 (m, 3.17 H, $CH_3\underline{CH_2CH_2}$), 2.85 (m, 1.66 H, CH_3CH_2-$CH_2\underline{CH_2}$), 4.90 (m, 1.48 H, $\underline{CH_2}CH_2COOCH_3$), 6.96 (t, 1.55 H, $\underline{CH_2}COOCH_3$), 7.92 (s, 3.00 H, $COO\underline{CH_3}$).

Methyl hexanoate from experiment with pent-1-ene-5-d_3 carried out at 5 atm p(CO): (int. TMS, solvent C_6D_6, $Eu(DPM)_3$): δ (ppm) 1.02 (t, 1.28 H, $\underline{CH_3}CH_2$), 1.63 (t, 1.82 H, $CH_3\underline{CH_2}$), 2.32 (m, 1.82 H, $CH_3CH_2\underline{CH_2}$), 3.81 (m, 1.55 H, $\underline{CH_2}CH_2COOCH_3$), 5.39 (t, 1.53 H, $\underline{CH_2}COOCH_3$), 6.54 (s, 3.00 H, $COO\underline{CH_3}$).

Analysis of the residual olefin from the hydroformylation of propene-3-d_3

The gases from the autoclave were bubbled into a solution of Br_2 in CCl_4 at 0°C and the resulting solution analyzed by NMR (int. TMS, solvent CCl_4): δ (ppm) 1.84 (m, 0.64 H, $\underline{CH_3}CHBr$), 3.65 (m, 1.53 H, $CHBr\underline{CH_2}Br$), 4.15 (m, 0.83 H, $\underline{CH}BrCH_2Br$).

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