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HYDROFORMYLATION OF DEUTERATED OLEFINS IN THE PRESENCE OF COBALT CATALYSTS

I *. EXPERIMENTS AT HIGH PRESSURE OF CARBON MONOXIDE

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Summary

The distribution of deuterium in the hydroformylation products of ω-deuterated α-olefins is consistent with a reaction mechanism involving initial formation of an olefinic catalyst π-complex. The role of the intermediate complexes in the formation of the products in the hydroformylation of but-1-ene-4-d_3 has been evaluated.

Introduction

In order to gain more information about the olefinic catalyst complexes which enable the olefin to form various isomeric products in cobalt-catalyzed hydroformylation, we have extended our studies of hydroformylation of ω-deuterated α-olefins to but-1-ene-4-d_3, pent-1-ene-5-d_3 and hex-1-ene-6-d_3.

By determining the deuterium contents of the products and its distribution between the various carbon atoms, it is possible to obtain information about the ability of such complexes to exchange hydrogen with the reaction gases, to promote isomerization of the complexed olefin, to promote intermolecular hydrogen transfer in the substrate, and to release isomerized olefin. It is also possible from the data to determine the extent of the formylation at the various carbon atoms of the substrate. Previously published data [1—4] only provide evidence for a substantial retention of deuterium in the hydroformylation products of deuter-

* Preliminary results see ref. 18.

TABLE 1

HYDROFORMYLATION OF LINEAR α-OLEFINS. (olefin 2 g; $Co_2(CO)_8$ 0.25 g; solvent 25 ml; $p(H_2)$ 80 atm; $p(CO)$ 80 atm; T 100°C)

Olefin	% formylation of the various carbon atoms in positions						R [a] (%)
	1	2	3	4	5	6	
$CH_3CH=^{14}CH_2$ [5]	48.0	20.0	32.0	—	—	—	40.0
$CD_3CH_2CH=CH_2$	69.0	14.0	6.0	11.0	—	—	13.7
$CD_3(CH_2)_2CH=CH_2$	71.2	14.4	3.3	2.3	8.8	—	11.0
$CD_3(CH_2)_3CH=CH_2$	73.8	[b]	3.3		[b]	6.4	8.0

[a] R = ratio between the amount of linear aldehyde derived from the carbonylation of the methyl group of the olefin and the total amount of linear aldehydes. [b] Total formylation in position 2 + 5 is 16.5%.

ated olefins and indicate a fairly rapid isomerization of the olefin in the olefinic catalyst complex resulting in a 1,2-hydrogen shift [1].

The results reported below were obtained in the first examples of hydroformylations carried out at a relatively high pressure of carbon monoxide and hydrogen; in these conditions no isomerized free olefin is formed before 2/3 of the starting olefin has undergone hydroformylation.

Results

In agreement with previous observations we found complete retention of deuterium in the products [1—4]. In Table 1 we show the extent of formylation of the various carbon atoms of the olefins tested, it is clear that all the carbon atoms have been formylated.

Table 2 lists the numbers of hydrogen atoms and (by difference) of deuterium atoms present on the carbon atoms of the straight-chain esters derived from the corresponding hydroformylation products of the olefins. Deuterium is absent from carbon atom 4 of methyl pentanoate, carbon atoms 4 and 5 of methyl hexanoate, and carbon atoms 4, 5, and 6 of methyl heptanoate. In other words, deuterium is present only on carbon atoms 2, 3, and ω of the esters.

The isomeric distribution of the products does not vary with the degree of olefin conversion during the hydroformylation under a relatively high partial pressure of carbon monoxide ($p(CO) > 50$ atm at 100°C), as already noted [6].

TABLE 2

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

Olefin	Number of hydrogens on carbon atoms					
	2	3	4	5	6	7
$CD_3CH_2CH=CH_2$	1.73	1.86	2.00	0.41	—	—
$CD_3(CH_2)_2CH=CH_2$	1.75	1.87	2.03	2.00	0.35	—
$CD_3(CH_2)_3CH=CH_2$	1.84	1.92	2.00	4.00		0.24

Furthermore the distribution of deuterium on the chain remains unchanged, as shown from the results obtained when the reaction of but-1-ene-4-d_3 was interrupted at various degrees of conversion. The residual olefin recovered after 30% conversion had the same deuterium distribution as the starting material.

Discussion

The results reported in Table 1 agree fully with those previously obtained for propene-1-^{14}C. Thus all the carbon atoms of the olefinic chain undergo hydroformylation and the extent of formylation of the ω-carbon atom decreases as the length of the olefinic chain increases.

The presence of deuterium on one of the carbon atoms of the olefin does not affect the isomeric composition of the products *.

The mechanism we proposed previously [5] to rationalize the formation of isomeric aldehydes in hydroformylation of olefins accounts satisfactorily for the new results. The distribution of hydrogen between the various carbon atoms of the straight-chain reaction products, as reported in Table 2, is in keeping with that mechanism. The absence of deuterium in position 4, 4, 5 and 4, 5, 6 in *n*-pentanal, *n*-hexanal, and *n*-heptanal, respectively, is consistent with the isomerization of an olefinic cobalt carbonyl hydridic complex which can isomerize by the mechanism suggested [5], but does not decompose to set free the olefin and the cobalt carbonyl hydride or deuteride. If it did decompose in this way the deuterium could appear also in the above mentioned positions. Two further consequences would also have been detected, viz. (a) the presence of isomerized free olefin during the hydroformylation and (b) the transfer of deuterium from the olefin to the gaseous phase, resulting in a loss of deuterium from the products.

By monitoring of the infrared spectrum of a solution of cobalt tetracarbonyl deuteride under "oxo" conditions (CO/H_2 1/1 80 atm, 100°C), we have shown that free cobalt carbonyl deuteride rapidly exchanges deuterium for hydrogen in the reaction vessel. In the absence of such behaviour for the hydroformylation of olefins under relatively high partial pressures of carbon monoxide, we conclude that once the olefinic catalyst complex which enables the olefin to form the various aldehydes is formed, it releases the organic substrate only in the form of an aldehyde.

A further consequence of the absence of free cobalt carbonyl hydride under "oxo" conditions when an excess olefin is present (that is during hydroformylation) is that the reduction of acylcobalt carbonyls must be performed by hydrogen, as suggested by Heck [8], and not by cobalt carbonyl hydrides as proposed by Van Boven et al. [9].

The contribution of each π-olefinic catalyst complex to the formylation of each carbon atom of the olefinic chain of but-1-ene may be evaluated from the analyses of the hydroformylation products of but-1-ene-4-d_3. These can be calculated by assuming (i) that the various reaction products are formed from the olefinic catalyst complexes as represented in Scheme 1, and (ii) that (as considered above), the isotopic effects do not influence the course of the reaction.

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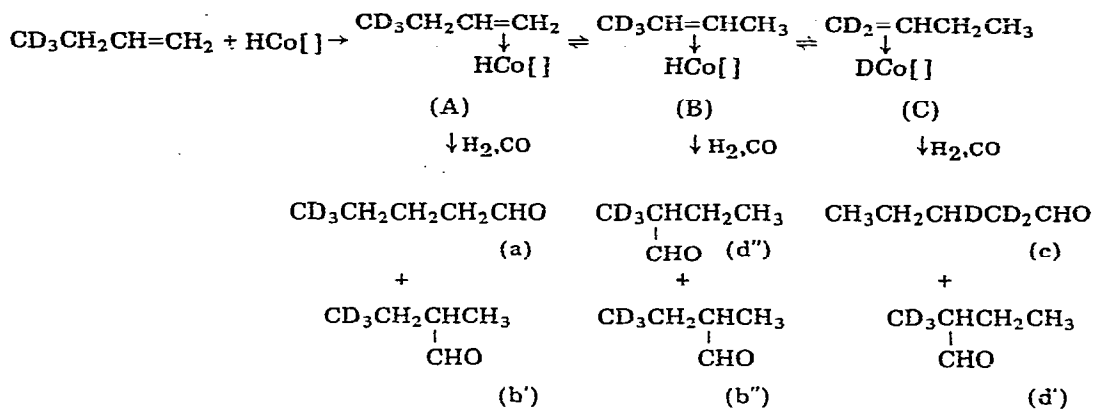
* The absence of isotopic effects in the hydroformylation of deuterated olefins in the presence of cobalt catalyst has also been noted [7].

SCHEME 1



Experimental results		Relationships	Calculated values
CD_3	→ $CD_3CH_2CH_2CH_2CHO$ 69%	b" = d"	b' = 9.5%
CH_2	→ $CD_3CH_2CH(CH_3)CHO$ 14%	b' + b" = 14	b" = d" = 4.5%
CH	→ $CD_3CH(C_2H_5)CHO$ 6%	d' + d" = 6	d' = 1.5%
CH_2	→ $CH_3CH_2CHDCD_2CHO$ 11%	$\frac{a}{b'} = \frac{c}{d'}$	

The ratio between the amounts of straight-chain and 2-methyl-substituted aldehydes derived from both complexes A and C is 7.3. This value is much higher than that observed in the hydroformylation of propene [6]. It is noteworthy that in the hydroformylation of non-deuterated but-1-ene there was a ratio of 4 between the amounts of straight-chain and the 2-methyl-substituted aldehyde. Evidently the replacement of a hydrogen atom by a methyl group on carbon atom 3 of propene has a significant influence in directing the introduction of a formyl group on the olefinic chain. This is in agreement with results observed for methyl-substituted α-olefins since the less branched aldehyde is produced in greater amount the greater the hindrance in the region of the double bond [10, 11]. The aldehyde derived from complex B is only 9% of the total aldehydes but 45% of the total 2-methylbutanal. This last point must be kept in mind when trying to explain the low asymmetric induction obtained in the formation of 2-methylbutanal by hydroformylation of butenes with chiral cobalt catalyst complexes [12]. Different complexes by undergoing *cis* addition of a Co—H bond to a C=C bond may give isomers of different chirality.

Experimental

GLC analyses were performed on a Perkin—Elmer F30 instrument. The isomeric mixtures of esters were separated by preparative GLC using a Perkin—Elmer F21 instrument.

NMR Spectra were recorded on a Varian T60 or a Perkin—Elmer R32 spectrometer. Mass spectra were recorded on a Perkin—Elmer 270B instrument.

Hydrogen distributions were determined by integration of the NMR spectra of solutions of esters in CCl_4 or C_6D_6 using $Eu(DPM)_3$ as shift reagent. The methyl group of the $COOCH_3$ moiety was used as an internal standard.

Materials

Tetradeuteromethanol: Merck product (99% isotopic purity).

Tetradeuteroacetic acid: Sorin product (99.6% isotopic purity).

Bromomethane-d_3. PBr_3 (271 g) was added slowly to CD_3OD (70 g) at 0°C. The mixture was then heated at 30°C and the evolved vapour was bubbled through a 20% Na_2CO_3 solution then over $CaCl_2$ and were then condensed by cooling to —80°C. The bromomethane-d_3 (101 g, b.p. 4.5°C) thus obtained showed no hydrogen absorption in its NMR spectrum.

1-Bromopropane-3-d_3. This was prepared as described by Bianchi et al. [13] for the synthesis of bromoethane-2-d_3. Propan-1-ol-3-d_3 [13] (44.7 g) and PBr_3 (96 g) gave 1-bromopropane-3-d_3 (36.5 g, b.p. 70°C, n_D^{25} 1.4309). NMR $\delta_{TMS}^{CCl_4}$: 1.85 ppm (t, 2.00 H, $CD_3\underline{CH_2}$), 3.40 ppm (t, 2.00 H, $\underline{CH_2}Br$).

But-1-ene-4-d_3. This was prepared by a procedure similar to that described by Hurd et al. [14] for the undeuterated compound.

The Grignard reagent prepared from CD_3Br (43.5 g) and Mg (14 g) in dibutyl ether (500 ml) was treated with allyl bromide (140 g) at 70°C. The evolved gases were condensed by cooling at —80°C to give but-1-ene-4-d_3 (15.5 g). NMR $\delta_{TMS}^{CCl_4}$: 2.03 ppm (m, 2.00 H, $CD_3\underline{CH_2}$), 4.93 ppm (m, 2.00 H, $CH=\underline{CH_2}$), 5.80 ppm (m, 1.00 H, $\underline{CH}=CH_2$).

Pent-1-ene-5-d_3. This was prepared by a procedure similar to that for but-1-ene-4-d_3, from ethyl bromide-2-d_3 [13] (56 g), Mg (13 g), dibutyl ether (400 ml) and allyl bromide (74 g). The crude product, purified by spinning band distillation, gave pent-1-ene-5-d_3 (15.3 g, b.p. 30°C, n_D^{20} 1.3715). NMR $\delta_{TMS}^{CCl_4}$: 1.39 ppm (t, 2.00 H, $CD_3\underline{CH_2}$), 2.04 ppm (m, 2.00 H, $\underline{CH_2}CH=$), 4.77 ppm (m, 2.00 H, $CH=\underline{CH_2}$), 5.81 ppm (m, 1.00 H, $\underline{CH}=CH_2$).

Hex-1-ene-6-d_3. This was made by a procedure similar to that described by Whitmore et al. [15]. The Grignard reagent prepared from 1-bromopropane-3-d_3 (26.8 g) and Mg (5.8 g) in diethyl ether (400 ml) was treated with allylbromide (28.7 g) and the mixture refluxed for 24 h. The crude product, purified by spinning band distillation, gave hex-1-ene-6-d_3 (8.7 g, b.p. 63°C, n_D^{20} 1.3876). NMR $\delta_{TMS}^{CCl_4}$: 1.33 ppm (t, 4.00 H, $CD_3\underline{CH_2}\underline{CH_2}$), 2.01 ppm (m, 2.00 H, $\underline{CH_2}CH=$), 4.91 ppm (m, 2.00 H, $CH=\underline{CH_2}$), 5.76 ppm (m, 1.00 H, $\underline{CH}=CH_2$).

Hydroformylation of olefins and identification of products.

Olefins were hydroformylated as described previously [16]. The conditions used are shown in Table 1. For butene, toluene was used as solvent, but in the other cases benzene was used.

Aldehydes were converted into the methyl esters of the corresponding acids in the usual manner [16]. The esters were analyzed and separated by GLC.

The results obtained are reported in Tables 1 and 2.

NMR spectra

Methyl pentanoate, $\delta_{TMS}^{CCl_4}$ ($Eu(DPM)_3$): 1.11 (t, 0.41 H, $\underline{CH_3}CH_2$), 2.25 (t, 2.00 H, $CH_3\underline{CH_2}$), 3.46 (m, 1.86 H, $C_2H_5\underline{CH_2}$), 4.91 (t, 1.83 H, $\underline{CH_2}COOCH_3$), 6.09 (s, 3.00 H, $COO\underline{CH_3}$).

Methyl 2-methylbutyrate, $\delta_{TMS}^{CCl_4}$ ($Eu(DPM)_3$): 2.85 (t, 0.91 H, $\underline{CH_3}CH_2$), 4.23 (d, 2.11 H, $\underline{CH_3}CH$), 5.02 (m, 2.09 H, $CH_3\underline{CH_2}$), 7.23 (m, 0.89 H, $\underline{CH}COOCH_3$), 7.96 (s, 3.00 H, $COO\underline{CH_3}$).

TABLE 3

MASS SPECTRA (20 eV) OF THE METHYL ESTERS DERIVED FROM THE HYDROFORMYLATION PRODUCTS OF DEUTERATED OLEFINS

Ester		Relative intensity of peaks			m/e
		M	*M* + 1	*M* + 2	
Methyl pentanoate	deuterated	100	30.00	—	119
	non deuterated [a]	100	7.10	—	116
	calculated	100	6.75	0.59	116
Methyl hexanoate	deuterated	100	14.80	—	133
	non deuterated [a]	100	8.30	—	130
	calculated	100	7.87	0.67	130
Methyl heptanoate	deuterated	100	16.70	—	147
	non deuterated [a]	100	11.10	1.30	144
	calculated	100	8.98	0.76	144

[a] Spectra obtained with non deuterated reference products.

Methyl hexanoate, $\delta^{C_6D_6}_{TMS}$ (Eu(DPM)$_3$): 1.10 (t, 0.35 H, $\underline{CH_3}CH_2$), 1.78 (t, 2.00 H, $CH_3\underline{CH_2}$), 2.71 (m, 2.03 H, $C_2H_5\underline{CH_2}$), 4.64 (m, 1.87 H, $\underline{CH_2}CH_2COOCH_3$), 6.61 (t, 1.75 H, $\underline{CH_2}COOCH_3$), 7.59 (s, 3.00 H, $COO\underline{CH_3}$).

Methyl 2-methylpentanoate, $\delta^{C_6D_6}_{TMS}$ (Eu(DPM)$_3$): 1.19 (t, 0.48 H, $\underline{CH_3}CH_2$), 2.00 (m, n.d., $CH_3\underline{CH_2}$), 2.30 (d, 2.52 H, $\underline{CH_3}CH$), 3.20 (m, n.d., $\underline{CH_2}CH$), 4.19 (m, n.d., $\underline{CH}COOCH_3$), 5.27 (s, 3.00 H, $COO\underline{CH_3}$).

Methyl heptanoate, $\delta^{C_6D_6}_{TMS}$ (Eu(DPM)$_3$): 0.96 (t, 0.24 H, $\underline{CH_3}CH_2$), 1.65 (m, 4.00 H, $CH_3\underline{CH_2}CH_2$), 2.85 (m, 2.00 H, $C_3H_7\underline{CH_2}$), 4.90 (m, 1.92 H, CH_2COOCH_3), 6.96 (t, 1.84 H, $\underline{CH_2}COOCH_3$), 7.92 (s, 3.00 H, $COO\underline{CH_3}$).

The intensities in the mass spectra of M + 1 and M + 2 peaks relative to the parent peak M are shown in Table 3.

Deuterium—hydrogen exchange between $DCo(CO)_4$ and H_2 under pressure in hydrocarbon solution.

A cold (—20°C) solution of $DCo(CO)_4$ in *n*-heptane (0.200 g $DCo(CO)_4$ in 50 ml C_7H_{16}) was placed in a cool rocking autoclave (150 ml capacity) which was then pressured first with CO to 40 atm and then with H_2 to 80 atm. The autoclave was connected to an IR cell capable of withstanding high pressure and heated to 80°C. The IR spectrum of the solution was continuously monitored by passing the solution slowly through a high pressure IR cell which was connected to the autoclave and kept under the same conditions. The IR spectra in the 2200—600 cm^{-1} region were recorded. There was a progressive increase in intensity of the band at 702 cm^{-1} attributable to the Co—H bending motion at the same time as a decrease in intensity of the band at 600 cm^{-1} attributable to the Co—D bending motion [17].

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