165. Hydroformylation of 1,1,1-d₃-2-Butene.
Isotope Effect on the Product Composition

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Summary

In the hydroformylation of 1,1,1-trideuterio-2-butene with $Rh_4(CO)_{12}$ the deuterated pentanals formed contain 75% of 5,5,5-trideuterio-pentanal, the rest being substantially 2,2-dideuterio-pentanal. On the contrary, using $Co_2(CO)_8$ as the catalyst precursor, position 1 and 4 are formylated to the same extent.
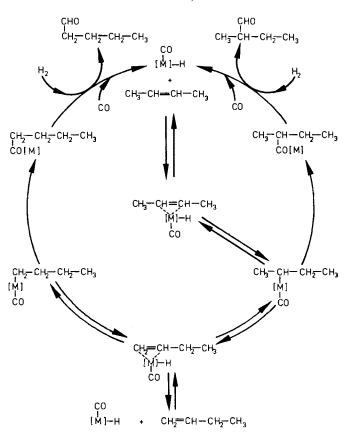
The formation of n-aldehydes from internal olefins with rhodium and cobalt catalysts is believed [1–3] to occur in both cases according to a preliminary sequence of addition of a M–H group to the olefin followed by M–H elimination until the n-alkyl metal carbonyl is formed. This complex then gives rise to the straight chain aldehyde by carbon monoxide insertion and hydrogenolysis *(Scheme 1)*. This mechanism, however, has been questioned in the case of the cobalt catalyst when hydroformylation is carried out under high carbon monoxide partial pressure in view of the experimentally proved stability of secondary alkylcobalt carbonyls under the above conditions [3–5] at least below 120°.

In order to obtain further information on the synthesis of straight chain aldehydes from $\varDelta^2$-olefins, 1,1,1-d₃-2-butene has been hydroformylated. It is known that in the elimination of olefins from deuterated complexes of rhodium and iridium a primary isotopic effect exists [6] [7]. In the hydroformylation of 1,1,1-d₃-2-butene such an effect is expected to cause a remarkable difference in the formylation rate in 1 and 4 positions. Therefore I and IV are expected to form in different amounts *(Scheme 2)*. If a kinetic isotopic effect in the migration of the double bond occurs according to the above postulated mechanism [1–3], a shift of the isomeric products composition toward the branched isomer should exist and should be detectable if a sufficient amount of n-aldehyde is formed.

A *cis/trans* mixture of 1,1,1-d₃-2-butene (*cis/trans* = 1.46) has been obtained through an iron catalysed cross-coupling reaction of d₃-methyl magnesiumiodide and 1-bromopropene [8]. This mixture has been hydroformylated using $Co_2(CO)_8$

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Scheme 1[a])

CHO
CH₂–CH₂–CH₂–CH₃

CHO
CH₃–CH–CH₂–CH₃

CO
[M]–H
+
CH₃–CH=CH–CH₃

H₂   CO   CO   H₂

CH₂–CH₂–CH₂–CH₃
CO[M]

CH₃–CH–CH₂–CH₃
CO[M]

CH₃–CH=CH–CH₃
[M]–H
CO

CH₂–CH₂–CH₂–CH₃
[M]
CO

CH₃–CH–CH₂–CH₃
[M]
CO

CH₂=CH–CH₂–CH₃
[M]–H
CO

CO
[M]–H   +   CH₂=CH–CH₂–CH₃

[a])   Double arrows mean reversibility but do not imply achievement of equilibrium conditions;

$$[M]-H = H_xM_y(CO)_{z-1}$$
with CO above [M].

Scheme 2

CH₃
|
CH
‖
CH
|
CD₃

$\dfrac{\text{H}_2, \text{CO}}{\text{catalyst}}$

CH₃–CH₂–CH₂–CD₂–CHO   (I)

CH₃–CH₂–CH–CHO
                |
               CD₃   (II)

CD₃–CH₂–CH–CHO
                |
               CH₃   (III)

CD₃–CH₂–CH₂–CH₂–CHO   (IV)

or $Rh_4(CO)_{12}$ as catalyst precursor. For comparison non deuterated 2-butene was hydroformylated under similar reaction conditions *(Table 1)*.

The reaction products were transformed into the corresponding methyl esters as previously described for other hydroformylation products [9]. The esters were separated through preparative gas chromatography and analysed by NMR. in the presence of $Eu(DPM)_3$ [10] and by mass spectroscopy. Furthermore the esters were transformed in the corresponding anilides by standard procedure [11] and the anilides analysed by mass spectroscopy. The results of the analysis are reported in *Tables 2–4*.

In the rhodium catalysed hydroformylation of $1,1,1-d_3-2$-butene position 4 has been formylated about three times more rapidly than position 1 *(Table 3 and 4)*. Correspondingly the amount of linear aldehyde is smaller by about 25% than that observed in the case of the unlabelled substrate *(Table 1)*. No detectable intra-molecular or intermolecular deuterium scrambling is apparent, more than 90% of the products arising from formylation in position 1 containing two deuterium atoms in a position with respect to the formyl group *(Table 3 and 4)*. From comparison of the data in *Tables 2–4* it can be concluded that the product arising from formylation

Table 1. *Hydroformylation of* cis-butene[a]) *and of 1,1,1-d_3-2-butene[a]) by* $Co_2(CO)_8$[b]) *and* $Rh_4(CO)_{12}$[c]) *in mesitylene[d]) at 100°*

Substrate	Catalyst Precursor	p_{H_2}[e]) (atm)	p_{CO}[e]) (atm)	Reaction time (h)	Con-version[f]) %	n-pentanal[f])[g]) %
cis-Butene	$Rh_4(CO)_{12}$	100	100	17	88	13 ± 0.6
	$Co_2(CO)_8$	94	406	4	40	60 ± 3
1,1,1-d_3-2-Butene	$Rh_4(CO)_{12}$	100	100	24	95	8.4 ± 0.4
(cis/trans = 1.46)	$Co_2(CO)_8$	100	400	6	60	61 ± 3

[a]) Olefin $\simeq$ 3 g. [b]) $\sim$ 1 g. [c]) 0.20 mg. [d]) 20 ml. [e]) At the reaction temperature.
[f]) Mol of aldehydes per 100 mol of substrate. Determined through gas-chromatography using cyclohexane ($\simeq$ 1 g) as internal standard.
[g]) Determined through gas-chromatography in the presence of toluene as internal standard. The relative error in the values of the straight chain aldehyde determination are $\pm$ 5%.

Table 2. *Deuterium content (%)[a]) of the anilides obtained from the primary hydroformylation products* via *the corresponding methyl esters*

Catalyst	Hydroformylation product considered	d_0	d_1	d_2	d_3	d_4	d_5	MDN[b])
$Co_2(CO)_8$	2-Methylbutanal	–	0.2	2.9	92.0	3.7	1.2	3.03
	n-Pentanal	0.3	1.5	6.8	91.4	–	–	2.89
$Rh_4(CO)_{12}$	2-Methylbutanal	0.3	0.5	3.2	96.0	–	–	2.95
	n-Pentanal	0.8	2.3	22.9	72.4	1.1	0.5	2.72
Deuterium content of the substrate (1,1,1-d_3-2-butene)								

[a]) Estimated accuracy $\pm$ 3%. [b]) Average number of deuterium atoms per molecule.

in position 1 contain only two deuterium atoms instead of three. The loss of deuterium from the substrate, to which corresponds formation of HD in the gas phase indicates that the reaction of rhodium carbonyl hydride species with hydrogen proceeds at a rate higher than the hydroformylation rate. Work is in progress to establish if to the isotope effect on products composition corresponds an overall kinetic isotope effect in rhodium catalysed hydroformylation.

Surprisingly in the case of the cobalt catalysed reaction the amount of formylation at 1 and 4 position is practically the same, as shown *(Table 4)* by the deuterium content on the δ C-atom and by the NMR. signal pattern (a clean triplet). Furthermore no difference is noticed in the isomeric composition of the reaction products starting with deuterated and undeuterated substrates. Contrarily to the case of the rhodium catalysed reaction only a very small deuterium loss from the substrate has been detected *(Table 2)* and practically no intermolecular deuterium exchange occurs. However, an intramolecular deuterium shift is shown by the fact that, according to the mass spectrum *(Table 3)*, about 50% the products originated from formylation at 1 position contains only one deuterium atom in the α-position with respect to the formyl group. More than 50% of the deuterium missing in position 2 *(Table 4)* is shifted to position 3, where instead of 25% of deuterium, as expected for a single 1,2-deuterium shift, about 30% of deuterium is found. The deuterium distribution in the branched product obtained with the cobalt catalyst fits with that which would be expected if most of the aldehyde were to arise

Table 3. *Percent[a]) of molecules of methyl-n-pentanoate containing the moiety* $-CXY-COOCH_3$ *(X, Y = H or D)*

	Catalytic System	
	$Co_2(CO)_8$	$Rh_4(CO)_{12}$
$-CH_2-COOCH_3$	52	75
$-CHD-COOCH_3$	25	2
$-CD_2-COOCH_3$	23	23

[a]) Calculated on the basis of the relative intensities in the mass spectrum of the peaks corresponding to the fragments $CX_2 = C\langle^{OH}_{OCH_3}$ originated by *McLafferty* rearrangement.

Table 4. *Average distribution of hydrogen atoms[a]) in the methyl esters obtained from the primary hydroformylation products*

Catalyst						MDN[b])
	CH$_3$ ——	CH$_2$ ——	CH$_2$ ——	CH$_2$ ——	COOCH$_3$	
$Co_2(CO)_8$	1.54	1.92	1.38	1.27		2.89
$Rh_4(CO)_{12}$	0.87	1.96	2.00	1.55		2.62
	CH$_3$ ——	CH$_2$ ——	CH ——	CH$_3$	COOCH$_3$	
$Co_2(CO)_8$	1.58	1.99	0.87	1.66		2.90
$Rh_4(CO)_{12}$	1.52	2.11	0.97	1.48		2.92

[a]) Determined by NMR. in the presence of $Eu(DPM)_3$ using the carbomethoxy group as internal standard. Estimated accuracy ± 5%.

[b]) Average number of deuterium atoms per molecule.

from a hydroformylation with no protium or deuterium shift. However, the slightly lower hydrogen content on the a C-atom, can be taken as an indication that a small part of the branched aldehyde arises after that a 1,2-deuterium shift has taken place.

The results obtained with the rhodium catalyst are in keeping with the present view on the formation of linear aldehydes from internal olefins. The isotope effect on product composition corresponds to that expected for the formation of 1-butene from a sec.-butyl-rhodium complex, on the base of literature data on the decomposition of iridium and rhodium complexes [6] [7] to olefin.

The lack of any observable isotopic effect in the case of cobalt can be due i) to a particular type of transition state [12] [13] or ii) to a compensation between a negative and a positive isotope effect [14] or iii) to a rapidly established equilibrium involving the splitting of an X-D bond (X = C, Co) preceding the rate determing step [12] or finally iv) to the formation of an unknown intermediate [3] not involving the breaking of C-D (or C-H) bonds, the decomposition of which back to a π-complex or to starting products is much slower than protium (or deuterium) migration with contemporary cobalt alkyl intermediate formation.

Both the lack of a large deuterium scrambling and the different isomeric compositions of the reaction products obtained by hydroformylating 1- and 2-butene are in contrast with an explanation of type iii). However, on the basis of the present data the choice between possibilities i), ii) and iv) appears to be unwarranted. Therefore no definite relationship between the lack of isotopic effect on products composition and the mechanism of formation of linear aldehydes in the presence of cobalt catalyst can be established. However, it is likely that important differences exist between the catalytic behavior of rhodium and cobalt complexes in some steps of the hydroformylation reaction.

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