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ON HYDROGEN ACTIVATION IN THE HYDROFORMYLATION OF OLEFINS WITH $Rh_4(CO)_{12}$ OR $Co_2(CO)_8$ AS CATALYST PRECURSORS

PIERO PINO, FELIX OLDANI and GIAMBATTISTA CONSIGLIO

Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology, Zürich (Switzerland)

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Summary

In the hydroformylation of ethylene with approximately equimolar H_2/D_2 mixtures and $Rh_4(CO)_{12}$ or $Co_2(CO)_8$ as the catalyst precursor about 50% of propionaldehyde-d_1 was formed. The propionaldehyde-d_0/d_2 ratio was ~ 3 for rhodium and ~ 2.6 for the cobalt catalyst. On the basis of the results and assuming that there is no rapid $M(H)_2/M(D)_2$ scrambling, activation of hydrogen through $M(H)_2$ or $M(H)_2$(olefin) complexes can be excluded.

Although about 45 years have elapsed since the discovery of hydroformylation [1], there is very little experimental information about the nature of the activation of hydrogen during the catalytic cycle, and the step in which that activation takes place; indeed, the nature of the species which activates hydrogen, leading to possible intermediates of the type [M]–H or $[M]\!<\!\begin{smallmatrix}H\\H\end{smallmatrix}$ is unknown.

For the cobalt-catalyzed reaction it was first postulated that hydrogen is activated by the previously known [2] reaction with $Co_2(CO)_8$ (reaction 1) [3–5]. On this interpretation a second molecule of $HCo(CO)_4$ was thought to be responsible for the final reduction of a acylcobalt complex to the aldehyde (reaction 2) [6,7].

$$Co_2(CO)_8 + H_2 \rightarrow 2HCo(CO)_4 \qquad (1)$$

$$RCOCo(CO)_4 + HCo(CO)_4 \rightarrow RCHO + Co_2(CO)_8 \qquad (2)$$

In contrast, other authors, mostly on the basis of kinetic evidence, suggested [12–15] the reaction of an intermediate dinuclear olefin complex with hydrogen to give the aldehyde (reaction 3) or the formation of dihydride π-olefin complex (reaction 4).

$$[Co_2(CO)_7(Olefin)] + H_2 \rightarrow \tfrac{1}{2}[Co(CO)_3]_4 + RCHO \qquad (3)$$

$$Co_2(CO)_8 + Olefin + H_2 \xrightarrow{-CO} [Co_2(CO)_7(Olefin)H_2] \xrightarrow{2CO} Co_2(CO)_8 + RCHO \qquad (4)$$

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More recently, activation of hydrogen by oxidative addition to an acylcobalt carbonyl (reaction 5) has been proposed [16], with $Co_2(CO)_8$ thus excluded from the catalytic cycle.

$$RCOCo(CO)_3 + H_2 \rightleftarrows RCOCo(CO)_3(H)_2 \qquad (5)$$

The mechanism of hydrogen activation in the rhodium-catalyzed hydroformylation has been even less investigated. For $RhH(CO)(PPh_3)_3$ as the catalyst precursor Wilkinson et al. [17] adapted the mechanism proposed by Breslow and Heck [18] for the cobalt-catalyzed reaction, but explicitely postulated the activation of hydrogen via an oxidative addition of hydrogen to a coordinatively unsaturated acylrhodium carbonyl complex (reaction 6). However, they have also shown that activation of hydrogen very easily occurs in the presence of a bimetallic complex (reaction 7) [19],

$$[RCORh(CO)(PPh_3)_2] + H_2 \rightarrow (RCORh(H)_2(CO)(PPh_3)_2 \qquad (6)$$

$$[Rh(CO)_2(PPh_3)_2]_2 + H_2 \rightarrow 2RhH(CO)_2(PPh_3)_2 \qquad (7)$$

by a reaction similar to that presented in eq. 1. For $Rh_4(CO)_{12}$ as the catalyst precursor, Markó et al. [20] postulated a reaction of hydrogen with an acylrhodium carbonyl intermediate (reaction 8), thus excluding $Rh_4(CO)_{12}$ or other rhodium carbonyls from the catalytic cycle. However, the same authors postulate the possibility of an activation of hydrogen by $Rh_4(CO)_{12}$ (reaction 9). The presence of an hydridic species of the type $HRh(CO)_3$ indicates the possibility of a reduction of the acylrhodium carbonyl without the formation on an acyl-dihydride intermediate, in a reaction similar to that in eq. 2.

$$Rh(CO)_3(COR) + H_2 \rightarrow RhH(CO)_3 + RCHO \qquad (8)$$

$$Rh_4(CO)_{12} + 2H_2 \rightarrow 4RhH(CO)_3 \qquad (9)$$

An inspection of reactions 1–9 shows that reactions 3 and 4 imply that both hydrogen atoms involved in the formation of one aldehyde molecule arise from the same hydrogen molecule whereas, the other schemes (1 and 2, 5, 6 and 7, 8 and 9) imply that the two hydrogen atoms arise wholly (schemes 5, 6, 8) or mainly (schemes 1, 7, 9) from different hydrogen molecules.

Hydroformylation reactions carried out with H_2/D_2 mixtures [21] should distinguish between the two sets of hypotheses (reactions 3 and 4 vs. reactions 1 and 2 or 5 for cobalt and 6, 7 and 9 for rhodium), if, under hydroformylation conditions H_2/D_2 or $M(H)_2/M(D)_2$ scrambling (leading to formation of H–D) occurs only to a limited extent. In the first case (reactions 3 and 4) only d_0- and d_2-labelled products should be formed, whereas in the second case (reactions 1, 2, 5, 6 and 7, 8 and 9) the substantial formation of d_1-labelled products is expected, in an amount consistent will the initial H_2/D_2 ratio after allowance for the kinetic isotope effect.

In the present work we first proved that with $Co_2(CO)_8$ or $Rh_4(CO)_{12}$ as the catalyst precursor substantially no H_2/D_2 scrambling takes place during hydroformylation. Analysis of the label in the reaction products then allowed us to exclude as a main path a mechanism in which both hydrogen atoms added in hydroformylation arise from the same molecule. Thus activation of hydrogen in reactions of types 3 and 4 must be excluded for both catalytic systems unless rapid $M(H)_2/M(D)_2$ scrambling occurs under the reaction conditions.

TABLE 1

HYDROFORMYLATION OF ETHYLENE WITH H_2/D_2 MIXTURES IN THE PRESENCE OF $Co_2(CO)_8$ OR $Rh_4(CO)_{12}$[a]

Run	Catalyst precursor	C_2H_4 (mmol)	H_2+D_2 (mmol)	Reaction time (h)	H_2, D_2 and HD content (%)[b]						Conversion to aldehyde[e] (%)
					Initial[c]			Final[d]			
					H_2	HD	D_2	H_2	HD	D_2	
1	$Co_2(CO)_8$	580	349	7.2	51.9	1.5	46.6	49.8	3.8	46.4	12
2	$Co_2(CO)_8$	230	250	6.0	50	-	50	n.d.	n.d.	n.d.	22
3	$Co_2(CO)_8$	211	334	5.8	~ 0	~ 0	100	n.d.	n.d.	n.d.	35
4	$Rh_4(CO)_{12}$	438	376	5.2	55.2	0.4	44.4	49.7	2.2	49.1	24
5	$Rh_4(CO)_{12}$	403	496	7.5	37.8	0.2	62.0	35.0	2.6	66.7	35

[a] Reaction conditions: 100°C and 100 atm P(CO): 50 ml n-pentane as the solvent. $Co_2(CO)_8$ 124 mg, $Rh_4(CO)_{12}$ 0.24 mg; volume of the reaction vessel 150 ml. [b] Determined on a MS-CEC-A-620 spectrometer; accuracy better than 0.5%. [c] Present in the gas phase before the beginning of the reaction. [d] Present in the gases released after the reaction. [e] Refers to ethylene; determined by gas chromatography using n-butanal as internal standard.

Results

The hydroformylation reactions were carried out with ethylene as the substrate in order to avoid the formation of isomeric mixtures of aldehydes, which would complicate the quantitative determination of the deuterium content in the products. As shown in Table 1, formation of H–D during hydroformylation is not significant under the conditions used. Furthermore no deuterium was found in the recovered ethylene within the limits of MS detection, showing that no exchange takes place between hydrogen atoms present in the substrate and in the gas phase at rates comparable to hydroformylation.

The H_2/D_2 molar ratio decreases during the reaction. A larger decrease was observed in the rhodium- than in the cobalt-catalyzed reaction (partly due the higher conversion in the latter case, Table 1), showing the existence of a overall isotope effect of 1.2 ± 0.3 for the cobalt- and of 1.7 ± 0.1 for the rhodium-containing catalytic system. The deuterium content of the reaction products and the distribution of the deuterium atoms in the propanal formed are shown in Table 2. The deuterium content was determined by reducing the aldehyde with $LiAlH_4$ and treating the propanol with *p*-methylbenzoyl chloride to give the corresponding propyl *p*-methylbenzoate, which was analyzed by mass spectroscopy. NMR spectroscopy was used to determine the average labelling at each aldehyde position; for these determinations we used not only the propyl *p*-methylbenzoate but also propionaldehyde dimethylacetal and propyl methanesulfonate in order to improve the reliability of the deuterium distribution data. In Table 3 the results obtained for all three derivatives of propionaldehyde from run 4 are shown as examples.

TABLE 2

ISOTOPE DISTRIBUTION IN THE GAS PHASE AND IN THE REACTION PRODUCTS FROM HYDROFORMYLATION OF ETHYLENE WITH H_2/D_2 MIXTURES

Run	Catalyst precursor	D_2/H_2[a] (molar ratio)		Isotopic distribution[b] in the propionaldehyde			Protium content at each[c] carbon atom in the propionaldehyde		
		Before the reaction	After the reaction	d_0	d_1	d_2	CH_3	CH_2	CHO
1	$Co_2(CO)_8$	0.90	0.93	37.8	46.6	14.6	2.74	1.91	0.53
2	$Co_2(CO)_8$	1.0	n.d.	36.7	45.1	16.5	2.76	1.84	0.52
3	$Co_2(CO)_8$	> 100	n.d.	2.5	3.6	89.0[d]	2.34	1.57	0.11
4	$Rh_4(CO)_{12}$	0.80	0.95	40.3	46.2	13.5	2.62	2.07	0.59
5	$Rh_4(CO)_{12}$	1.644	1.90	21.0	48.2	30.3	2.39	2.01	0.42

[a] Values accurate to ±0.02. [b] Calculated from the mass spectra of the propyl *p*-methylbenzoate obtained with a Hitachi–Perkin Elmer RMU-6L spectrometer. Values are estimated to be accurate within ±2% (absolute). [c] Estimated accuracy ±5% (relative). Determined from the NMR (Bruker WH 90) spectra of propionaldehyde dimethylacetal, propyl methanesulfonate and propyl *p*-methylbenzoate using the protons of the introduced groups as the internal standard. The data for the $Rh_4(CO)_{12}$ experiment are the average of the spectra of all three derivatives and for the $Co_2(CO)_8$ experiment of the last two derivatives. [d] ~ 4.9% d_3 labelled aldehyde is also present.

TABLE 3

NMR ANALYSES OF VARIOUS DERIVATIVES OF PROPIONALDEHYDE ARISING FROM RUN 4; PROTIUM CONTENT AT EACH CARBON ATOM [a]

Derivative	Protium content at each carbon atom of propionaldehyde		
	CH_3	CH_2	CHO
$CH_3CH_2CH(OCH_3)_2$	2.67	2.09	0.59
$CH_3CH_2CH_2OSO_2CH_3$	2.60	2.11	0.57
$CH_3CH_2CH_2OCOC_6H_4CH_3$	2.58	2.01	0.61
Mean	2.62	2.07	0.59

[a] Calculated using the protons of the introduced group as the internal standard.

TABLE 4

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED ISOTOPIC DISTRIBUTIONS IN THE PROPIONALDEHYDE ON THE BASIS OF PROPOSED MECHANISMS

	k_H/k_D	d_0	d_1	d_2
Calculated according to eq. 3 or 4	1	50	0	50
	1.5	60	0	40
	2	66.6	0	33.3
Calculated according to eq. 1, 2, 5–9	1	25	50	25
	1.5	36	48	16
	2	44.4	44.4	11.1
Experimentally found for $Co_2(CO)_8$	1.2 ± 0.1 (1.6 ± 0.1) [a]	37.8	46.6	14.6
Experimentally found for $Rh_4(CO)_{12}$	1.7 ± 0.1 (1.7 ± 0.1) [a]	40.3	46.2	13.5

[a] Overall isotope effect; figures are based on the H_2/D_2 composition in the gas phase before and after the reaction. Figures in brackets are based on the labelling of propionaldehyde: $k_H/k_D = \sqrt{d_0/d_2}$.

Discussion

In Table 4 the observed isotopic distribution in propionaldehyde and the experimentally found isotope effect are compared with the isotopic distribution calculated by assuming hydrogen activation according to reaction 1 or 5 and 8 or 9. The calculations were made by assuming isotopic effects equal to 1, 1.5 and 2, in the above steps in which the H_2 (or D_2) molecules are split irreversibly. The amount of d_1-labelled products found cannot be reconciled with reaction via processes 3 and 4 which should give no d_1-products, whatever the isotopic effect. In contrast the data very closely correspond to those expected for reactions 1, 5, 8 and 9 assuming an overall isotope effect of between 1.5 and 2. The overall isotope effect calculated from the labelling of propionaldehyde is equal to that calculated from the gas phase composition in the case of rhodium (1.7 ± 0.1 vs. 1.7 ± 0.1) and a little higher in the case of cobalt (1.6 ± 0.1 vs. 1.2 ± 0.3). However, in the latter case, the value calculated from the gas phase composition is less accurate because, due to the low conversion, the difference between starting and final composition of the H_2/D_2

mixtures is small. The data do not allow a choice between reactions 1 and 6 or 2 and 7 for activation of hydrogen. However, the very small extent of H_2/D_2 scrambling shows that, if activation of hydrogen occurs by reaction 1 and 9, the reverse reaction must be slower than hydroformylation.

The analysis for deuterium at each position in propionaldehyde shows the presence of this isotope at position 2 for cobalt but not for rhodium. On the basis of the hydroformylation mechanism [18] proposed by Breslow and Heck, under the conditions used carbon monoxide insertion and acyl reduction should be more rapid than β-hydrogen elimination from the alkylmetal/complex when $Rh_4(CO)_{12}$ is the catalyst precursor, whereas, in the case of $Co_2(CO)_8$, β-hydrogen elimination should be much faster than π-olefin complex dissociation [23]. The equilibrium for scrambling of deuterium with the substrate, as determined in a separate experiment involving deuterioformylation of ethylene (Tables 1 and 2), is approached but not reached, and so the rate of β-hydrogen elimination must be of the same order of magnitude as that of CO insertion and aldehyde formation (Scheme 1).

SCHEME 1

$$\mathrm{H[M](CO) + (olef.)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{H[M](CO)(olef.)}$$

$$\mathrm{H[M](CO)(olef.)} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{R[M](CO)}$$

$$\mathrm{R[M](CO)} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{[M]COR} \cdots \rightarrow \mathrm{RCHO}$$

$$\mathrm{Rh}: k_3 \gg k_{-2}$$

$$\mathrm{Co}: k_3 \sim k_{-2} \sim k_2 > k_{-1}$$

Experimental

Further experiments are in progress to clarify the most favourable path for hydrogen activation in the catalytic cycle of hydroformylation, which in our opinion, still remains largely unknown despite some statements in recent literature [6,8,9].

VPC analyses were performed with a Perkin–Elmer Sigma 4 chromograph equipped with an FID detector. NMR spectra were recorded at 90 MHz with a WH90 Bruker spectrometer using $(CH_3)_4Si$ as the internal standard. The mass spectra of the derivatives of the aldehydes were recorded with a Hitachi Spectrometer RMU-6L, and those of the $H_2/HD/D_2$ mixtures with a MS-CEC-A-620 instrument.

Pentane was distilled over $LiAlH_4$ before use. D_2 was supplied by Carbagas AG, Zürich; H_2 and C_2H_4 by Sauerstoff- und Wasserstoff-Werken AG, Luzern. $Co_2(CO)_8$ [24] and $Rh_4(CO)_{12}$ [25] were prepared by published methods. Carbon monoxide was prepared by catalytic decomposition of formic acid; purity > 99.5%. Other reagents were Fluka products and were used without further purification.

Hydroformylation reactions

These were carried out in stainless steel autoclaves (150 ml) in pentane as solvent at 100°C using standard procedures [26]. After 12–25% conversion (evaluated from gas absorption) the autoclave was cooled and the residual gases released into a gasometer. The exact determination of the degree of conversion was made by VPC analysis for propionaldehyde using n-butanal as standard. Propionaldehyde was immediately reduced with $LiAlH_4$ and converted into propyl *p*-methylbenzoate or methanesulfonate by standard procedures [27] in yields of ~ 70–80%. Part of the reaction solution from hydroformylation was flash distilled and the propionaldehyde was converted in its dimethylacetal in methanol containing ammonium nitrate [28] (yield ~ 65%).

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