Rhodium-catalyzed hydrocarbonylation of acetic acid into higher acids

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Abstract

The hydrocarbonylation of acetic acid into higher homologues catalyzed by rhodium/iodide systems has been investigated at 20 MPa and 220°C. In homogeneous catalysis the most convenient precursor proved to be $[RhI_2(CO)_2]^-$ prepared from $[RhCl(CO)_2]_2$ in the presence of LiI; mean turnover frequencies of 67 h^{-1} and selectivities as high as 80% in propionic acid were obtained. In addition, in heterogeneous catalysis, rhodium supported upon activated carbon was observed to be an efficient system for the conversion of acetic acid into propionic acid (80% selectivity) in a fixed bed reactor. The reaction mechanism is thought to be an iodoacetyl rather than an ethanol pathway in the homogeneous system, while the two seem likely to be in operation in the heterogeneous system. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The production of C_2 oxygenates and higher alcohols or acids starting from raw materials such as synthesis gas or methanol, represents an attractive challenge provided one single product can be selectively produced. If we exclude the hydroformylation of olefins, which requires the previous production of an alkene, or the direct oxidation of hydrocarbons and the direct synthesis of C_1–C_6 alcohols from synthesis gas, which give mixtures of products, there are only a small number of processes which meet these requirements.

From CO/H_2, heterogeneous rhodium catalysts have been reported to selectively afford ethanol [1,2]. To a lesser extent rhodium catalysts promoted with iridium, manganese oxide and alkali metals were shown to directly produce acetic acid [3–7]. Carbonylation of methanol catalyzed by $[RhI_2(CO)_2]^-$ in the presence of iodides as promoters was developed

on an industrial scale by Monsanto and gives rise to selectivities higher than 99% with regard to methanol [8]. Recent improvements of this process have been patented by British Petroleum [9] and Hoechst Celanese [10]. Iridium compounds in particular have been claimed to be active soluble catalysts to carbonylate methanol to acetic acid [9,11]. Many attempts have been reported in the literature to heterogenize the catalytic system either in batch or in fixed bed reactors [8]. Generally the catalysts comprise rhodium supported upon various polymers [12] for liquid phase reactions or on activated carbon [13,14], various inorganic acids [15,16], or zeolites [17,18]. The reaction is carried out at higher temperatures in the vapour phase. In such conditions an iodide promoter remains necessary while the proposed mechanism [19,20] is similar to that assumed for homogeneous catalysis [11]. On these various supports, operating in conditions approaching those of the homogeneous process, numerous heavier acids were produced. A significant increase in the pressure (> 20 MPa), the temperature (250°C), as well as the introduction of synthesis gas instead of carbon monoxide [15] resulted in large amounts of C_3, C_4 and C_5 carboxylic acids with a classical Anderson–Schulz–Flory (ASF) distribution (ca. 20% w/w propionic acid).

The production of a single C_n carboxylic acid by homologation of the C_{n-1} acid or its corresponding ester has a limited reference within the literature [21–25] since a few papers deal with the high pressure homogeneous catalysis in the presence of ruthenium, rhodium, nickel or palladium complexes with an iodide promoter. Among these catalytic systems, ruthenium/iodide mixtures afforded the best results, although the catalytic activity was limited to 8 h^{-1} at 46 MPa, and 220°C [24]. Furthermore, to the best of our knowledge, we present here the first approach in heterogeneous catalysis of the homologation reaction by hydrocarbonylation of carboxylic acids or esters.

This paper reports on the selective preparation of propionic acid by hydrocarbonylation of

acetic acid either by homogeneous catalysis starting from various rhodium/iodide precursors or by heterogeneous catalysis using a 2% (w/w) Rh/activated carbon catalyst prepared by an Organometallic Chemical Vapor Deposition method [26].

2. Experimental part

2.1. Catalyst preparation

[RhCl(CO)$_2$]$_2$ [26], [AsPh$_4$][RhI$_2$(CO)$_2$] [27], [Rh(CO)$_2$(acac)] [28] and [Rh$_4$(CO)$_{12}$] [29] complexes were prepared using published methods.

The complex [RhI$_3$(CO)(dppp)] was prepared as follows: 1.74 mmol (450 mg) of [Rh(CO)$_2$(acac)] was dissolved, under a nitrogen atmosphere, in 70 ml of methanol at 20°C. One equivalent of 1,3-bis(diphenylphosphino) propane was added to the stirred solution together with 60 ml of acetic acid and 5 ml of a 57% solution of hydriodic acid. Immediate precipitation of a dark orange powder occurred. This precipitate was filtered, washed with dry ether and dried under reduced pressure. Recrystallization (dichloromethane–hexane) at −25°C yielded the air stable complex as thin dark red needles (yield 85%). Infrared (KBr pellets): ν_{CO} 2084 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, δ: ppm): 7.1–8.1 (m, 20H), 3.6 (2H), 2.02 (2H), 2.12 (2H). ^{31}P^1{H}NMR (CD$_2$Cl$_2$, δ: ppm): −0.59 (d), $J_{Rh-P} = 96$ Hz.

Full details of the preparation of the supported rhodium catalyst by an organometallic chemical vapour deposition method have been reported elsewhere [26]. Typically, vapours of the complex [RhCl(CO)$_2$]$_2$, diluted in a helium–hydrogen mixture, were contacted with activated carbon maintained in a fluidized bed. The duration of the deposit was adjusted to obtain 2% (w/w) Rh on activated carbon. This one-step method permitted the production at low temperature (125°C) of well-dispersed metallic rhodium aggregates. The activated car-

bon used in this study is commercially available (Aldrich), it possesses a BET area of 725 m^2 g^{-1}, and was used without further activation or modification of its surface properties. EDS analysis revealed the presence of traces of sulphur, and of small amounts (total ca. 1%) of various metals ([Fe] $\approx$ [Cu] > [Cr] $\approx$ [Ni]). The rhodium catalyst prepared by this method contained 2% Rh (w/w) (as determined by both atomic absorption and ICP) and possessed a mean particle size of 3 nm (CO chemisorption measurements).

2.2. Homogeneous catalytic tests

The homogeneous hydrocarbonylation of acetic acid was performed in a Hastelloy-B2 100-ml autoclave, equipped with a 500-ml ballast vessel to maintain a constant reaction pressure. The reactor was charged with 180 mmol acetic acid, 6.2 mmol of hydriodic acid (1.4 g of a 57% solution in water) and 1.48 10^{-4} g at of rhodium. After purging with nitrogen, the pressure was fixed at 10 MPa (CO/H$_2$ = 2) and, when the temperature of 220°C was reached (15 min), the pressure was adjusted to 20 MPa. The stirring (1500 rpm) was maintained for the entire run (6 h). Following a slow decompression of the reactor, the liquid products were analyzed on a Carlo Erba GC 6000 gas chromatograph equipped with a 50 m CPWAX 58CB (i.d.: 0.32 mm) column or by GC/MS (Perkin-Elmer QMASS 910). The gaseous products were analyzed on a Perkin–Elmer Autosystem GC.

2.3. Heterogeneous catalytic tests

The catalytic tests were performed in a stainless steel (Z2CND17-12) reactor of 8 mm i.d. which was lined by copper 6 mm inner diameter. The length of the heated element was 0.43 m and the catalyst was maintained in the central section of the reactor by glass wool plugs. The CO/H$_2$ mixture was prepared in the laboratory and controlled by G.C. (TCD detector). The syngas was compressed to 70 MPa in a 500-ml high pressure vessel. The pressure of the device was regulated by a Tescom 70 MPA, the gas flow measured by a Setaram 3100 Flowmeter and regulated by an electronic controller coupled with a Brooks 5835N electrovalve. At the exit of the reactor the liquids were trapped at 10°C under high pressure. The pressure of the exit gas was reduced to 2 MPa and the gas phase was analyzed by G.C. with both TCD and FID detectors. The CH$_3$OH–CH$_3$I mixture or acetic acid–alkyl iodide mixture was cooled to 0°C to avoid evaporation and introduced into the device by a model 303 Gilson metering pump. Prior to the catalytic test, the catalyst (0.5 g) was reduced by pure hydrogen (2 l h^{-1} g$_{cat.}^{-1}$) during heating from room temperature to 230°C (2°C min^{-1}) and then 15 h at 230°C. The hydrogen was then released and the synthesis gas was introduced progressively. Catalytic activities were compared on the basis of methanol or acetic acid (molar %) remaining in the final mixture. Indeed, it has been shown that, under the present experimental conditions, some acetic acid can be formed by carbonylation of some methanol produced by reaction of CO and H$_2$ upon the rhodium catalyst.

3. Results and discussion

3.1. Homogeneous catalytic study

For the homogeneous hydrocarbonylation of acetic acid the activity of various catalysts was examined, and aqueous HI was selected as the iodide-containing promoter. A total syngas pressure of 20 MPa was maintained during all of the catalytic run at a constant temperature of 220°C. The best catalytic activity was observed for a CO/H$_2$ molar ratio of 2. The different molar ratios of [CH$_3$COOH]/[Rh], [CH$_3$COOH]/[HI], and [HI]/[Rh] were respectively 1215, 29 and 42, in order to be near to the conditions required for the low pressure methanol carbonylation reaction, mainly for the concentrations of the promoter. Table 1 presents the conversion of acetic acid and the yields in C$_3$–C$_5$ acids for

Table 1
Acetic acid hydrocarbonylation

Rhodium catalysts	TOF (h^{-1})	Conversion acetic acid (%)	Carboxylic acid yield (mol %)[a]			
			C_3	n-C_4	iso-C_4	C_5
$RhCl_3 \cdot 3H_2O$	12	6	96.3	total 3.7		−
$[AsPh_4][RhI_2(CO)_2]$	22	11	77.8	9.7	12	0.5
$[RhCl(CO)_2]_2$	42	21	81	8.9	9.8	0.3
$[Rh(CO)_2(acac)]$	34	17	49.9	21.1	25.2	3.5
$[Rh_4(CO)_{12}]$	26	13	95.8	total 4.2		−
$[RhI_3(CO)(dppp)]$	46	23	95.6	total 4.4		−

[a]Carboxylic acid yield with regard to acetic acid converted.
Reactives charge: rhodium 1.4 10^{-4} g at., HI 6.2 mmol, acetic acid 0.18 mol.
Typical operating conditions: 220°C, 2 MPa at the working temperature, CO/H_2 (2/1), 6 h.

the investigated catalysts, namely $RhCl_3 \cdot 3H_2O$, $[AsPh_4][RhI_2(CO)_2]$, $[RhCl(CO)_2]_2$, $[Rh(CO)_2(acac)]$, $[Rh_4(CO)_{12}]$ and $[RhI_3(CO)(dppp)]$.

From these results, it appears that the production of higher acids starting from acetic acid is a very selective process since almost no ester was produced for all the investigated systems. Indeed, the analysis of the liquid phase by GC/MS allowed us to identify, besides small amounts of iodine containing compounds $(C_2H_5I \gg CH_3I > C_3H_7I > C_4H_9I)$, only traces of ethanol and of the corresponding ethyl esters. However, the main competing reaction to rhodium-catalyzed acetic acid hydrocarbonylation is the water–gas shift (WGS) reaction as evidenced by a significant quantity of carbon dioxide present in the gaseous phase. Contrary to the ruthenium systems described by Knifton [24], which produced significant amount of ethane and propane, the analysis of the gaseous phase did not reveal hydrocarbon formation (only traces of methane were found). This could be due to the low partial pressure of hydrogen in the present conditions, but the main reason probably arises from the low hydrogenating character of the rhodium catalyst [11,19] compared to ruthenium. Although the stoichiometric ratio required for the homologation reaction is 0.5, the CO insertion step is probably rate-limiting since the highest conversions were obtained for a CO/H_2 ratio of 2. In addition, it should be mentioned that, after each catalytic run, significant quanti-

ties of insoluble rhodium were observed. In a separate experiment, it was verified that this 'rhodium black' precipitate did not induce any homologation of acetic acid under the operating conditions.

The compound $[Rh(CO)_2(acac)]$ appears to be the precursor permitting the widest homologation since 50% propionic acid, 46% butyric acid, and 4% pentanoic acid were produced. This system is efficient as regards the homologation reaction itself, but the desired selectivity in a single acid is not met. High selectivities in propionic acid were obtained starting from $RhCl_3 \cdot 3H_2O$ and $[Rh_4(CO)_{12}]$, this latter species encouraging twice the conversion of acetic acid with respect to the rhodium salt. In terms of selectivity, only 4% butyric acid was produced. Concerning the complex $[RhCl(CO)_2]_2$, it is known that the addition of hydriodic acid affords the species $H[RhI_2(CO)_2]$ [11]. For this reason we prepared the homologous complex $[AsPh_4][RhI_2(CO)_2]$. Surprisingly, bearing in mind that the same molar quantity of rhodium was introduced, $[RhCl(CO)_2]_2$ led to twice the activity of the pre-formed anionic complex, the various selectivities in C_3–C_5 acids being identical. In our opinion the difference in productivity stems from the nature of the counter ion, either H^+ or $[AsPh_4]^+$. Due to its steric hindrance, the cation $[AsPh_4]^+$ should present no interaction with the $[RhI_2(CO)_2]^-$ species, whereas H^+ may give rise to an ion-

Table 2
FTIR analysis of the rhodium solution after catalysis

Rhodium catalysts	ν_{CO} (cm^{-1})	Assignment
$RhCl_3 \cdot 3H_2O$	2090 (vs), 2035 (vw)	$[RhI_4(CO)_2]^-$
$[AsPh_4][RhI_2(CO)_2]$	2083 (vs)	–
$[RhCl(CO)_2]_2$	2094 (vs), 2071 (vs)	$[RhI_4(CO)_2]^-$, $[RhI_4(CO)]^-$
$[Rh(CO)_2(acac)]$	2090 (vs), 2030 (vw)	$[RhI_4(CO)_2]^-$
$[Rh_4(CO)_{12}]$	2090 (vs), 2070 (vs)	$[RhI_4(CO)_2]^-$, $[RhI_4(CO)]^-$
$[RhI_3(CO)(dppp)]$	2089 (vs)	$[RhI_3(CO)(dppp)]$

pairing interaction with the anionic rhodium sub-complex. The dramatic accelerating effect of Lewis acids upon CO insertion, including that of proton acids has previously been reported [30]. It is known that significant amounts of water are required in the Monsanto process to maintain the stability of the $[RhI_2(CO)_2]^-$ catalyst [10], this species being generated from various rhodium salts or complexes. In the present case, there is a competition between the rate of formation of the active species starting from $RhCl_3 \cdot 3H_2O$, $[RhCl(CO)_2]_2$, $[Rh(CO)_2(acac)]$ and $[Rh_4(CO)_{12}]$, and the rate of decomposition into insoluble materials due to the low water concentrations. Interesting results were also obtained with $[RhI_3(CO)(dppp)]$, where dppp is the ligand bis(diphenylphosphino)propane. In a recent paper, Moloy and Wegman [31] demonstrated the stabilizing effect of a diphosphine ligand upon a rhodium–ruthenium system for the reductive carbonylation of methanol to ethanol. Table 1 shows that a 23% conversion of acetic acid was achieved in 6 h and a high

selectivity in propionic acid (ca. 96%) was obtained. As compared with the other cases, little insoluble rhodium was found after the catalytic run: therefore this system appears to be attractive.

After the catalytic runs, infrared spectra were recorded. The results are displayed in Table 2. Infrared measurements for the dppp complex revealed that the single ν_{CO} at 2089 cm^{-1} belongs to the $[RhI_3(CO)(dppp)]$ species. Except for $[AsPh_4][RhI_2(CO)_2]$ which gave a ν_{CO} band at 2083 cm^{-1} that remains unassigned, the other systems gave rise to $[RhI_4(CO)]^-$ and $[RhI_4(CO)_2]^-$ which were identified by their ν_{CO} bands [32]. In a separate experiment, addition of HI to the complex $[AsPh_4][RhI_2(CO)_2]$ at room temperature in acetic acid afforded the complex $[AsPh_4][RhI_4(CO)]$. All attempts to isolate these two tetraiodorhodium (III) species from a catalytic solution by addition of $[AsPh_4]Cl$ or $[AsPh_4]I$ failed. The only dark red crystalline product isolated was proved by its X-ray crystal structure to be in fact $[AsPh_4]I_3$.

Starting from $[RhCl(CO)_2]_2$ it was determined that around 85% (w/w) of the rhodium introduced decomposed into insoluble rhodium. The stabilization of the generated species was particularly investigated. As in the carbonylation of methanol [10,11] or methyl acetate [33], the addition of increasing amounts of LiI was investigated. Adding up to 10–20 equivalents of LiI per rhodium led to the observation of an increase in catalytic activity (see Table 3). The highest value of the turnover frequency was

Table 3
Influence of the LiI concentration on the acetic acid conversion

[LiI]/[Rh]	TOF (h^{-1})	Acetic acid conversion (%)	Carboxylic acid yield (mole %)[a]			
			Propionic	iso-Butyric	*n*-Butyric	Pentanoic
no LiI	42	21	81	8.9	9.8	0.3
2	50	25	80.1	8.3	9.3	0.3
4	59	29	86.9	5.8	7.1	0.2
10	67	33	83.5	6.2	9.3	1
20	63	31	83.3	7.8	8.6	0.3
40	48	24	84.1	6.8	9.1	–

[a]Carboxylic acid yield basis acetic acid converted.

$67\ h^{-1}$, around eight times the value observed by Knifton [24] with a ruthenium catalyst. For higher concentrations of LiI the activity was reduced. While for $[LiI]/[Rh] = 10$, around 5% insoluble rhodium were found following a catalytic experiment, almost no insoluble material was detected at $[LiI]/[Rh] = 40$. For the carbonylation of methanol or methyl acetate, the effect of LiI has been frequently discussed, particularly by Fulford et al. [34]. The role of LiI is not only to stabilize the active species $[RhI_2(CO)_2]^-$ but also to exert a promoting effect upon the oxidative addition of CH_3I. After a catalytic run and a slow depressurization of the reactor, the solutions were analyzed by infrared. Two ν_{CO} bands were detected at 2093 and 2073 cm^{-1} and were assigned to $[Li(solvent)_n][RhI_4(CO)_2]$ and $[Li(solvent)_n]$ $[RhI_4(CO)]$ respectively, a slight shift being due to the changing in the cation species [32].

3.2. Heterogeneous catalytic study

From previous work dealing with the methanol carbonylation into acetic acid it appears that the activity of carbon supported metal catalysts follows the order: Rh > Ir > Ni > Pd > Co > Ru > Fe [35]. No significant synergic effect was observed upon the addition of a second metal to the active metallic phase. However, the use of activated carbon as a support allows to work at high temperature (250°C–285°C), with a stable activity over long reaction periods (500 h) [13]. The main role of this support is to promote the alkyl iodide oxidative addition to metal centres which have a low affinity for halides. This promoting effect could be explained by an electronic transfer between the support and the metal, resulting in an acceleration of the limiting steps of the carbonylation reaction [36].

In sharp contrast with supports such as La_2O_3 or SiO_2, the leaching of rhodium from the activated carbon supported catalyst during the methanol carbonylation reaction was much reduced. In addition, although the temperature was increased from 20°C with regard to the conditions previously used for silica [20], the 2% (w/w) Rh/C* catalyst displayed a constant activity during the 16–115 h investigated period, whereas we have observed that for a 2% (w/w) Rh/SiO_2 catalyst the catalytic activity decreased dramatically after 60 h. The anchoring of rhodium was greatly improved on activated carbon with regard to silica since after the catalytic tests the loss of metal was determined to be 35% from Rh/C* (115 h run) and 90% from Rh/SiO_2 (60 h run). Our results in a fixed bed reactor give strong evidence that the hydrocarbonylation is due to supported rhodium. Previous investigations in batch reactors had led the authors to observe a poor catalytic activity

Table 4
Hydrocarbonylation of methanol to higher acids on 2% Rh/C*

Reaction time (h)	Selectivity[a]						Productivity	
	AcMe	AcEt	C_2	C_3	C_4	C_5	$g\ g_{cat.}^{-1}\ h^{-1}$	$g\ g_{Rh}^{-1}\ h^{-1}$
16	2.2	3.2	79	14	1.6	0.2	0.49	24.5
24	0.2	1.6	81	15	2.0	0.1	0.58	29
41	0.7	1.2	81	15	2.2	0.1	0.50	25
49	–	1.7	80	16	2.2	0.1	0.48	24
65	–	1.5	79	17	2.6	0.1	0.45	22.5
73	0.4	1.5	79	17	2.3	0.1	0.57	28.5
89	0.4	1.4	78	17	2.6	0.1	0.57	28.5
97	0.3	1.3	78	17	2.6	0.1	0.53	26.5
115	0.5	1.4	78	18	2.6	0.2	0.61	30.5

[a]Selectivity basis on the product of the hydrocarbonylation (molar percentage, H_2O not included).
Operating conditions: $P = 21$ MPa, $T = 250$°C, $CO/H_2 = 60/40$, gas flow = $3\ l\ h^{-1}\ g_{cat.}^{-1}$, $CH_3OH/CH_3I = 7.7/1$ M, $CH_3OH + CH_3I = 0.2$ ml $h^{-1}\ g_{cat.}^{-1}$.

for Rh/C* catalysts and to conclude that it was due to homogeneous catalysis resulting from the rhodium leaching [37]. Concerning the La_2O_3 support, we observed not only a loss of rhodium but also a solubilisation of the support by acetic acid to afford lanthanum acetate.

In order to attain a significant chain growth the experiments were performed at 21 MPa and 250°C and for a duration of more than 100 h: the activity remained constant and no methanol was detected in the reaction mixture. The results obtained with a 2%Rh/C* are presented in Table 4.

A high selectivity in carboxylic acids (> 95%) was observed with particularly few esters being produced, and a significant chain growth (20% M). However, since large quantities of acetic acid were obtained, the chain growth remained too short and followed an ASF distribution. These results were in opposition to the anticipated selective production of propionic or butyric acids. In order to reach this objective a study of the direct hydrocarbonylation of acetic acid was undertaken. The catalytic results using the same 2% Rh/C* catalyst are summarized in Table 5. Under the same experimental conditions as for methanol it proved possible to prepare propionic acid with an excellent selectivity ($\approx$ 80%), butyric and pentanoic acids being al-

Table 5
Catalytic behaviour of 2% Rh/C* catalyst for acetic acid hydrocarbonylation

Reaction time (h)	Remaining AcOH[a]	Selectivity[b]				
		AcMe	AcEt	C_3	C_4	C_5
16	65	51.2	10.9	32.9	4.8	0.5
24	75	16.8	5.3	62.8	13.3	1.8
41	77	1.3	3.9	75.7	16.3	2.7
48	73	0.3	3	75.9	18.7	2.0
64	74	–	2.7	78.5	17.2	1.7
72	74	–	2.3	78.5	17.5	1.7
88	72	–	1.5	72.6	22.6	3.3

[a]Molar percentage.
[b]Selectivity calculated from the product of the hydrocarbonylation (molar percentage, H_2O not included).
Operating conditions: P = 21 MPa, T = 250°C, CO/H_2 = 60/40, gas flow = 3 1 h^{-1} g$_{cat.}^{-1}$, CH_3COOH/CH_3I = 7.7/1 M, $CH_3COOH + CH_3I$ = 0.2 ml h^{-1} g$_{cat.}^{-1}$.

Table 6
Catalytic behavior of 2% Rh/C* for hydrocarbonylation reactions

Reaction time (h)	Remaining substrate[a]	Selectivity[b]				
		AcMe	AcEt	C_3	C_4	C_5
14	76.3	13.9	27.2	52.9	5.6	0.3
23	79.5	–	12.6	77.6	9.3	0.8
38	77.4	–	8.5	79.9	10.8	1.6
45	79.1	–	10.4	76.9	11.6	0.9
15	71.7	–	18.3	69.9	11.4	0.3
24	74.3	–	7.7	78.4	13.4	0.6
30	77.9	–	4.2	77	16.7	0.7

[a]Molar percentage; the four first rows correspond to $CH_3COOH + C_2H_5I$, and the three last rows to $CH_3COOCH_3 + CH_3I$.
[b]Selectivity calculated from the products of the hydrocarbonylation (molar percentage, H_2O not included).
Operating conditions: P = 21 MPa, T = 250°C, CO/H_2 = 60/40, gas flow = 3 1 h^{-1} g$_{cat.}^{-1}$, substrate/RI = 7.7/1 M, substrate + RI = 0.2 ml h^{-1} g$_{cat.}^{-1}$.

most the 20% of products remaining. It is worth mentioning that an induction of ca. 24 h was required which corresponded to a stabilization and an activation period for the catalyst. During this initial period, significant amounts of esters (methyl- and ethyl acetate) were formed. Beyond this stage, the selectivity in higher acids as well as the activity (with respect to acetic acid), was practically constant. The productivity of the catalyst was around 0.1 g of higher acids per g cat.$^{-1}$ h^{-1}. Methanol needed to methyl acetate was provided both by carbon monoxide hydrogenation and methyl iodide hydrolysis. As methanol produced under the reaction conditions should afford very quickly methyl acetate, ethanol was presumably produced by acetic acid reduction instead of by direct homologation of methanol.

Concerning the activity of the supported catalyst it is well known that the presence of chlorine atoms has a significant poisonous effect in CO/H_2 reactions [38]. Such an effect was also observed here. Indeed, with a 2% (w/w) Rh/C* catalyst prepared by conventional impregnation of the support by $RhCl_3 \cdot 3H_2O$ (similar mean particle size of 4–5 nm), the productivity of carboxylic acids after an induction period of 24 h was significantly reduced: 85% remaining acetic acid, the product distribu-

tion being similar to that shown in Table 5. This classical catalyst contained around 20 at.% of chlorine whereas those prepared by OMCVD contained only 3–4 at.% remaining chlorine.

Under the same experimental conditions, it has also been verified that ethanol hydrocarbonylation also leads to both propionic and butyric–pentanoic acids (64% and 5% respectively), 14% of starting alcohol being unreacted. For this latter reaction, the activity of the catalyst was slightly lower than for methanol hydrocarbonylation yet higher than for acetic acid hydrocarbonylation. Substitution of methyl iodide by ethyl iodide led to the results presented in Table 6. In this case, while there was a decrease in the induction period the differences between the two iodides with respect to catalytic activity or selectivity into higher acids were not significant. The results obtained starting from either methyl acetate/methyl iodide or acetic acid/ethyl iodide were quite comparable for both activity and selectivity (Table 6) indicating the same mechanistic pathway for the two starting materials.

4. Mechanistic considerations

4.1. Homogeneous catalysis

Knifton [24] reported the high pressure ($\simeq 46$ MPa, 220°C) hydrocarbonylation of acetic acid with ruthenium homogeneous catalysts and proposed a catalytic cycle in which the key step is the formation of acetyl iodide. Oxidative addition, reduction of the acyl to an ethyl group, CO insertion and reductive elimination of propionyl iodide are the principal steps of this catalytic sequence.

In the present work, it is worth noting that significant amounts of CO_2, and therefore hydrogen, were produced by the water–gas shift reaction reducing the amounts of water in the medium. The hypothesis that acetic acid in the presence of hydriodic acid gives rise to acetyl iodide appears attractive. The small volumes of water introduced as the HI solution (57%) and

those formed during the reduction steps would be consumed by the WGS reaction, thus shifting the equilibrium shown in Eq. (1) towards the right.

$$CH_3COOH + HI \Leftrightarrow CH_3COI + H_2O \qquad (1)$$

In addition, at least in homogenous conditions, the formation of the acetato rhodium (I) or (III) species appears rather unlikely. Furthermore, as almost no ethyl propionate was detected in the reaction medium, the presence of ethanol as a starting material for propionic acid production seems equally unlikely. Finally, since the direct use of ethanol rather than acetic acid as reactant resulted in the formation of half as much propionic acid under the same experimental conditions, the ethanol route for the hydrocarbonylation of acetic acid may be discarded. Thus, presumably the acetyl species, produced by the oxidative addition of CH_3COI to the active rhodium species, is reduced by hydrogen to generate an ethyl rhodium species which give an acyl species in a CO insertion step. Recently, the $[(EtCO)Rh(CO)_2I_3]^-$ complex has been characterized during the carbonylation of ethylene reaction [39].

4.2. Heterogeneous catalysis

From previous work carried out using a Rh/Pr_6O_{11} catalyst [20], as well as from the literature results, it appears that the mechanisms involved in the methanol carbonylation are similar in homogeneous and heterogeneous catalysis [40,41]. Furthermore, it is known that the carbonylation of ethanol and higher alcohols is at least ten fold times slower than that of methanol [11,8]. While in homogeneous catalysis, the hydrocarbonylation mechanism of acetic acid is modelled largely on the alcohol carbonylation, this might not be the case for heterogeneous catalysis. Here the formation of acetate species must to be taken into account. Two routes might therefore be considered (Scheme 1).

(i) Hydrolysis of acyl iodide in acetic acid can occur which leads to its chemisorption on the catalytic surface and produces a carboxylate
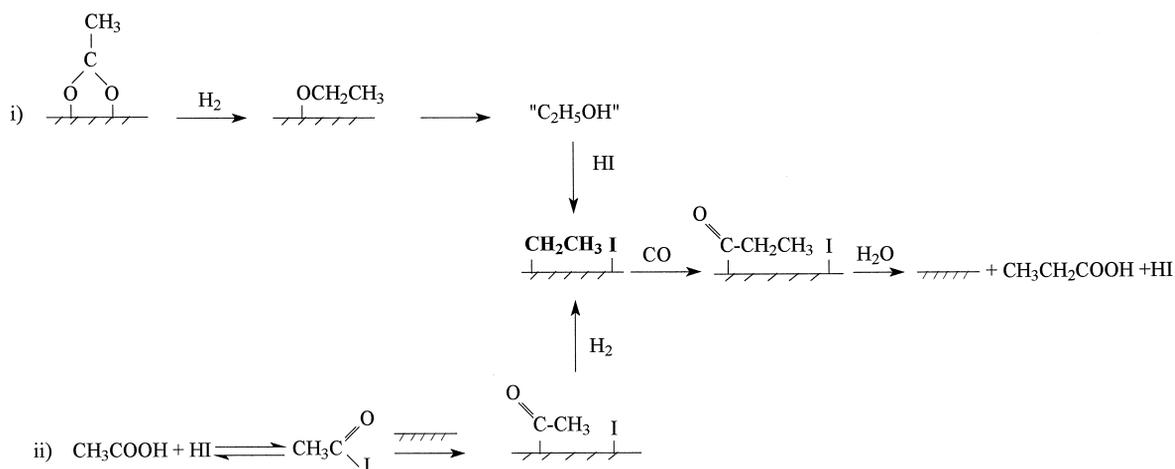
Scheme 1. Mechanistic pathway for the homologation of acetic acid.

species. The reduction of this acetate species to an alkoxy species has been widely studied for cobalt, nickel or iron heterogeneous catalysts on various supports (SiO_2, Al_2O_3, C...) [42], but Orita et al. [43–45] have concluded in their studies with CO/H_2 that the presence of the carboxylate species is essential for oxygenate (EtOH) formation. The reduction of acetate to alkoxy species could occur readily under the present experimental conditions. Ethanol formed through hydrogenolysis or hydrolysis of the ethoxy species could lead to the esterification of acetic acid into ethyl acetate or to propionic acid via ethanol carbonylation. Equally it was shown over 5% Rh/La_2O_3 (operating conditions of Table 5) that if ethanol leads to a selectivity comparable to that obtained from acetic acid (60–63% propionic acid), the activity would be higher (productivity in higher acids: 0.5 g cat.$^{-1}$ h^{-1} compared with less than 0.1 g cat.$^{-1}$ h^{-1}). The rate determining step could then be the reduction of carboxylates into alkoxy species, explaining the weaker reactivity of acetic acid compared to ethanol. This result is contrary to that obtained in homogeneous catalysis.

(ii) Alternatively, direct chemisorption of acyl iodide on the catalytic surface could occur to produce a [$CH_3CO–Rh–I$] species. Subsequent reduction would give rise to the ethyl species

[$CH_3CH_2-Rh–I$], which would insert rapidly carbon monoxide in agreement with the low quantities of ethyl iodide observed during the run.

The ethyl species could also be obtained via a facile dehydrogenation of ethanol, yielding ethylene and subsequently ethyl-Rh formation.

It is difficult to differentiate route (i) from route (ii) as illustrated by IR results following chemisorption over 5% Rh/Pr_6O_{11} of C_2H_5I, CO and H_2 (route i) or C_2H_5OH, CO and H_2 (route ii) and heating. In the two cases propionate species were characterized (propionate bands at 2980, 2944 (νCH_3); 1548 ($\nu_a CO$); 1470 ($\delta_a CH_3$); 1375, 1309, 1253 ($\delta_s CH_3$); 1079, 1028, 873, 803 cm^{-1} (CH_2). Moreover, in the two cases the νCO band at 1679 cm^{-1} seems to characterize a propionyl species in agreement with the band of an acyl group at 1624 cm^{-1} [20] and the band at 1679 cm^{-1} appearing after a propionaldehyde chemisorption. The presence of propionate and propionyl species was confirmed by chemical trapping experiments. Indeed, over the same catalytic surface (Rh/ Pr_6O_{11}), after the adsorption of C_2H_5I (or C_2H_5OH), CO, H_2 and the trapping by a great excess of CH_3I, methyl propionate and methyl ethyl ketone were characterized by gas chromatography. It is worth to mention that the support alone did not promote the formation of

these propionate and propionyl species, whereas the presence of acetate and formate species occurred, showing clearly that the presence of rhodium is necessary for chain growth.

All the results indicated the partial transformation of C_2H_5I into ethanol upon the surface. This was verified by IR, since after C_2H_5I chemisorption the ethoxy bands appeared at 2978, 2927, 2875 (νCH_3); 1475, 1442 (δCH_2); 1386 (δCH_3); 1148, 1097 (ν_a C–C); 1056 (νCO); 882 (ν_s C–C); 826, 793 and 718 and ethyl bands at 1209, 946 and 850 cm^{-1}. However, the CH_2 and CH_3 vibrations could not be differentiated between ethoxy or ethyl species. Due to the simultaneous presence of these two systems the discrimination between routes (i) and (ii) is unlikely. Presumably the two mechanisms should prevail.

Acknowledgements

References

[1] M. Ichikawa, Bull. Chem. Soc. Jpn. 51 (1978) 2268 and 2273.
[2] V. Ponec, Catal. Rev. Sci. Eng. 29 (1987) 183.
[3] T. Nakajo, K. Sano, S. Matsuhira, H. Arakawa, J. Chem. Soc., Chem. Comm. (1987) 647.
[4] R. Burch, M.I. Petch, Appl. Catal. A 88 (1992) 39.
[5] R. Burch, M.I. Petch, Appl. Catal. A 88 (1992) 77.
[6] H. Hamada, Y. Kuwahara, Y. Kintaichi, T. Ito, K. Wakabayashi, H. Iijima, K. Sano, Chem. Lett. (1984) 1611.
[7] Y. Sugi, K. Takeuchi, H. Arakawa, Chem. Lett. (1985) 1315.
[8] M.J. Howard, M.D. Jones, M.S. Roberts, S.A. Taylor, Catal. Today 18 (1993) 325, and references quoted therein.
[9] C.S. Garland, M.F. Giles, J.G. Sunley, Eur. Patent Appl. 0 643 034 A1 (priority 10.09.1993 to BP Chemicals).
[10] B.L. Smith, G.P. Torrence, A. Aguilo, J.S. Alder, US Patent 5 001 259 (priority 19.03.1991 to Hoechst Celanese).
[11] P.M. Maitlis, A. Haynes, G.J. Sunley, M.J. Howard, J. Chem. Soc., Dalton Trans. (1996) 2187.
[12] J. Hjortkjaer, Y. Chen, B. Heinrich, Appl. Catal. 67 (1991) 269.
[13] R.G. Schultz, P.D.D. Montgomerry, J. Catal. 13 (1969) 105.
[14] K.K. Robinson, A. Hershman, J.H. Craddock, J.F. Roth, J. Catal. 27 (1972) 389.
[15] E. Tempesti, A. Kiennemann, S. Rapagna, C. Mazzocchia, L. Guifre, Chem. Ind. (1991) 548.
[16] G. Ritter, G. Luft, Chem. -Ing. -Tech. 59 (1987) 485.
[17] M.S. Scurell, R.F. Howe, J. Mol. Catal. 7 (1980) 535.
[18] T. Yashima, Y. Orikasa, N. Takahashi, N. Hara, J. Catal. 59 (1979) 53.
[19] D. Forster, J. Chem. Soc., Dalton Trans. (1979) 1639.
[20] L. Chateau, J.P. Hindermann, A. Kiennemann, E. Tempesti, J. Mol. Catal. 107 (1996) 367.
[21] J.F. Knifton, Chem. Tech. (1981) 609.
[22] J.F. Knifton, Hydrocarbon Process. 60 (1981) 113.
[23] J.F. Knifton, J. Chem. Soc., Chem. Comm. (1981) 41.
[24] J.F. Knifton, J. Mol. Catal. 11 (1981) 91.
[25] J.F. Knifton, J. Mol. Catal. 16 (1982) 101.
[26] Ph. Serp, R. Feurer, R. Morancho, Ph. Kalck, J. Catal. 157 (1995) 294.
[27] L.M. Vallarino, Inorg. Chem. 4 (1965) 161.
[28] Y.S. Varshavskii, T.G. Cherkasova, Russ. J. Inorg. Chem. 12 (1967) 899, (Engl. Transl.).
[29] Ph. Serp, Ph. Kalck, R. Feurer, R. Morancho, Rhodium Express 9 (1995) 5.
[30] S.B. Butts, T.G. Richmond, D.F. Shriver, Inorg. Chem. 20 (1981) 278.
[31] K.G. Moloy, R.W. Wegman, Organometallics 3 (1989) 2883.
[32] B.T. Heaton, C. Jacob, S. Moffet, J. Organomet. Chem. 462 (1993) 347.
[33] J.R. Zoeller, V.H. Agreda, S.L. Cook, N.L. Lafferty, S.W. Polichnowski, D.M. Pond, Catal. Today 13 (1981) 278.
[34] A. Fulford, C.E. Hickey, P.M. Maitlis, J. Organomet. Chem. 398 (1990) 311.
[35] K. Kujimoto, K. Omata, T. Shikada, H. Tominaga, in: D.R. Fahey (Ed.), Industrial Chemicals via C_1 Processes, ACS Symp. Ser., 328 (1987) 208.
[36] H. Yagita, K. Fujimoto, J. Mol. Catal. 69 (1991) 191.
[37] M.E. Halttunen, M.K. Niemelä, A.O.I. Krause, A.I. Vuori, J. Mol. Catal. 109 (1996) 209.
[38] R.B. Anderson, The Fischer–Tropsch Synthesis, Academic Press, 1984.
[39] D.C. Roe, R.E. Sherida, E.E. Bunel, J. Am. Chem. Soc. 116 (1994) 1163.
[40] T.W. Decklewa, D. Forster, Adv. Catal. 34 (1986) 81.
[41] P.R. Ellio, J.M. Pearson, A. Haynes, H. Adams, N.A. Bailey, P.M. Maitlis, Organometallics 13 (1994) 3215.
[42] J. Cressely, D. Farkhani, A. Deluzarche, A. Kiennemann, Mat. Chem. Phys. 11 (1984) 413.
[43] H. Orita, S. Naito, K. Tamaru, J. Chem. Soc. Chem. Comm. (1984) 150.
[44] H. Orita, S. Naito, K. Tamaru, J. Catal. 90 (1984) 183.
[45] H. Orita, S. Naito, K. Tamaru, J. Phys. Chem. 89 (1985) 3066.