Hydrocarbonylation of linear and branched aliphatic C_2–C_4 alcohols catalyzed by cobalt–ruthenium systems. A comparative study

Gérard Jenner

Laboratoire de Piézochimie Organique, Chimie Organique Appliquée, EHICS, Université Louis Pasteur, 1, rue Blaise Pascal, 67008 Strasbourg (France)

(Received November 20th, 1987)

Abstract

In an extension of studies of the hydrocarbonylation of C_2–C_4 alcohols in the presence of a bimetallic catalyst system at high Syngas pressures to yield the next higher homologue, the effect of the catalytic system based on cobalt and ruthenium compounds promoted by iodine or iodides has been examined. For the optimal Co/Ru ratio the selectivity for the higher alcohol is highest because of a large decrease in the extent of hydrocarbon and ether formation. Neither this ratio nor the optimal pressure depends on the structure of the alcohol.

It is suggested that the synergism observed in Co–Ru-catalyzed hydrocarbonylation of alcohols is due to a cocatalytic effect of the Ru catalyst involving reaction of ruthenium hydrides with acyl-cobalt complexes. The mechanism is consistent with the suggestion that there is an intermediate olefin that undergoes hydroformylation in a subsequent step.

Introduction

Studies of hydrocarbonylation of alcohols to give the next higher alcohols (called homologation by Wender [1]), have dealt almost exclusively with the conversion of methanol to ethanol owing to its obvious economical interest, but unsatisfactory extents of conversion and selectivity have prevented commercial application of the process [2*].

The main industrial interest in alcohols lies in the fact that they are readily dehydrated to olefins (which are high-value chemicals) and in their possible use as additives to gasoline. This is especially true of butanols, which facilitate the dissolution of methanol in gasoline and also increase the tolerance to water of

---

* Reference number with asterisk indicates a note in the list of references.

methanol-hydrocarbons mixtures [3]. With the exception of tertiary or benzyl alcohols [4], homologation of alcohols other than methanol, however, could not be achieved satisfactorily.

Recently, we have shown that such alcohols can be transformed into their next homologues via hydrocarbonylation catalyzed by a mixed cobalt–ruthenium system that includes an iodide promoter [5–7]. The composition of the catalytic system, the pressure, the temperature and the gas composition are all important, and the reaction is under the direct influence of these parameters. The multimetallic catalyst introduces a synergistic effect in the homologation of alcohols and appears to be a good system for transforming other substrates [2,8–11]. This article considers general kinetic and selectivity aspects of the homologation of alcohols and proposes possible mechanistic pathways for the homologation of other substrates.

Experimental

The following experimental conditions were used unless otherwise specified: alcohol, 5.1 cm^3; catalyst 0.9 mmol of metal; iodine 1.5 mmol; temperature, 170 °C for ethanol reactions, 180 °C for propanol reactions, and 200 °C for butanol reactions; time, 2 h; H$_2$, 300 bar; CO, 150 bar. Details of kinetic procedures and analyses are given elsewhere [5–7].

Comparative study

The influences of the Syngas composition and temperature were investigated only in the case of ethanol. It was found that a CO/H$_2$ ratio between 0.5 and 1 (hence corresponding approximately to the stoichiometric ratio) was optimal for the synthesis of the next higher alcohol. Temperatures in the range 170–200 °C gave the highest yields, with temperatures higher than 200 °C leading to extensive formation of the corresponding ether and hydrocarbons. The most important parameters, however, are the composition of the catalytic system (catalyst and promoter) and the total pressure, and this study was focused on these aspects.

The hydrocarbonylation products include mostly alcohols (the target products), ethers and hydrocarbons. The amounts of the other side products, alkyl acetates, higher esters, a symmetrical ketone and formates (these last are formed only in the reactions involving ethanol and propanol) were usually small.

Influence of the catalyst composition

The best metal catalysts for the homologation of methanol involve cobalt compounds. The widely accepted mechanism for the reaction involves the activation of methanol by protonation and hence the unusually high acidity of HCo(CO)$_4$ is regarded as essential for the reaction.

Several authors suggested that addition of cocatalysts would increase the hydrogenation ability of the promoted cobalt catalyst. Ruthenium was found to be by far the best of those examined [12–15]. The studies produced no evidence for bimetallic catalytic functionality in these systems, the two metals apparently acting independently [15,16].

Promotion of homologation of methanol by iodine or iodides is well known. It was recently shown that the nature of the iodide promoter has a definite influence
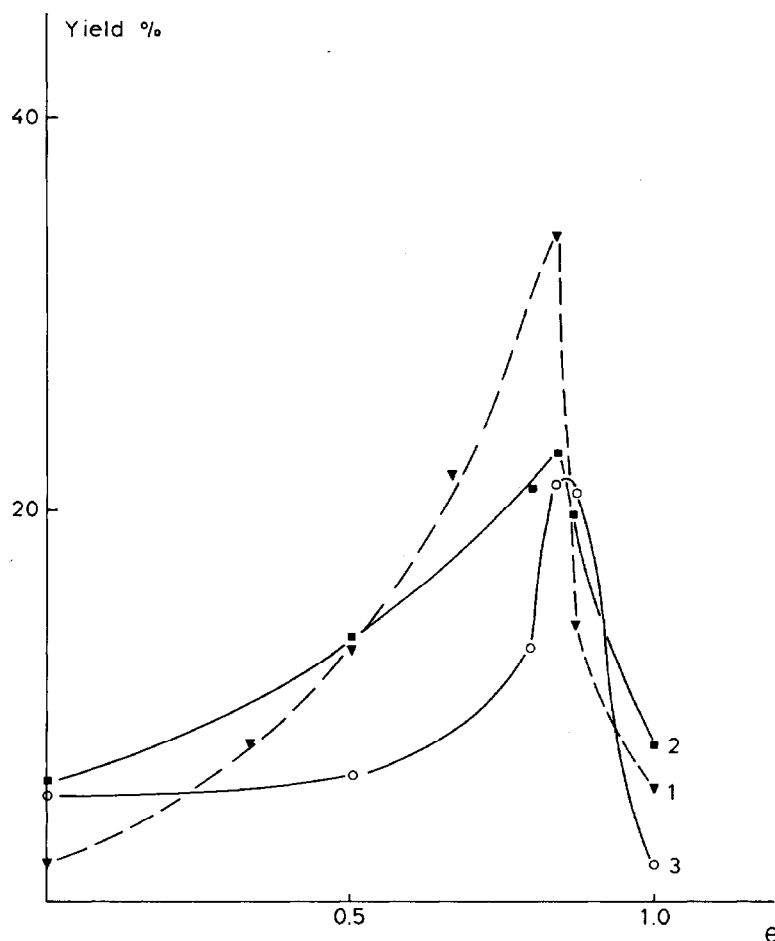
Fig. 1. Hydrocarbonylation of ethanol and propanols. Effect of the catalyst ratio $\theta([Co]/[Co+Ru])$ on the homologation products (standard conditions. Ethanol (1); 1-propanol (2); 2-propanol (3).

on the reaction rate, covalent iodides being much more active than ionic iodides [17]. Moreover, if both types of iodides are used simultaneously there is synergistic effect [17].

The above observations prompted us to consider for the activation of the homologation of alcohols a catalytic system formed from a mixture of a cobalt and a ruthenium compound associated with either iodine or an iodide or both. The aim was to control the balance between hydrogenation activity (leading to hydrocarbon formation) and carbonylation ability (favouring acids and esters).

(i) Effect of the Co/Ru ratio. The potential catalytic activity of the Co/Ru system was assessed from results of hydrocarbonylations carried out with various Ru/Co ratios, including separate runs with each metal. Figures 1 and 2 show the extent of formation of the next higher alcohol as a function of the catalytic composition (θ is the ratio $[Co]/[Co + Ru]$).

The Figures clearly show a large dependence of the yield of C_{n+1} products on the catalyst composition. Use of the cobalt or ruthenium catalyst separately gives in most cases (i.e. except for the tertiary alcohol, 2-methyl-2-propanol) only poor yields
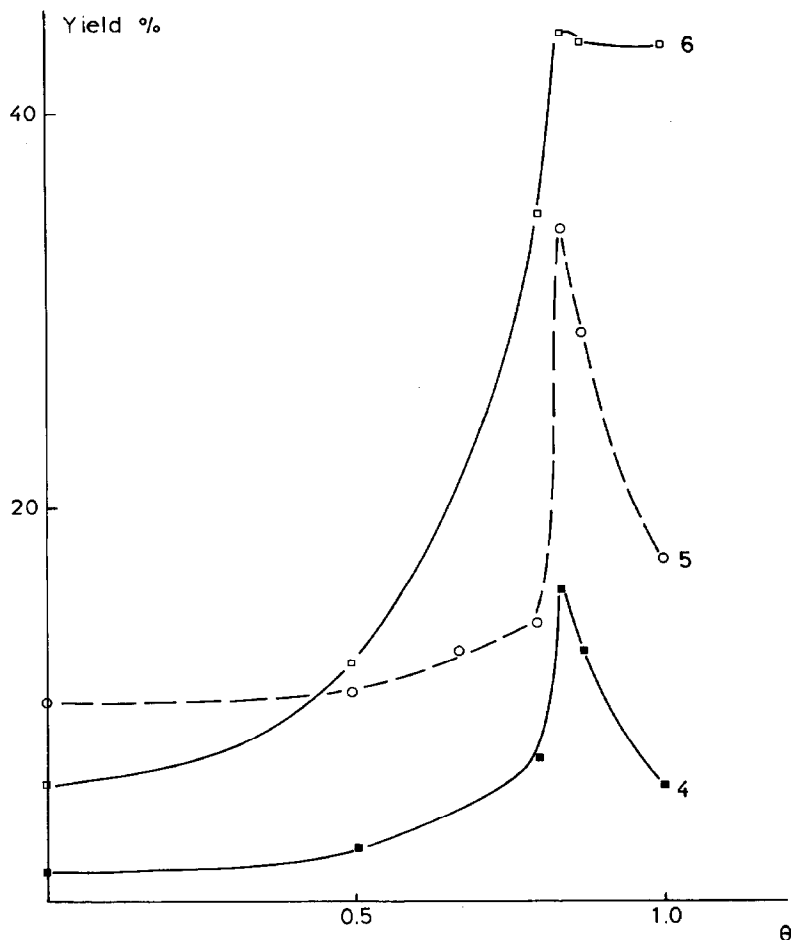
Fig. 2. Hydrocarbonylation of butanols. Effect of θ on the homologation products (standard conditions). 1-Butanol (4); 2-butanol (5); 2-methyl-2-propanol (6).

of the higher alcohol. Cobalt, and ruthenium both produce a high conversion of the starting alcohol, but most of the substrate undergoes dehydration to ether and/or is transformed into hydrocarbons, the relative amounts of ether and hydrocarbons depending on the starting alcohol (since ethers are readily formed from low molecular weight alcohols). It must be emphasized that ruthenium nevertheless shows a slight homologation activity, an observation consistent with the report that ruthenium carbonyl iodide systems can convert methanol into ethanol and even higher alcohols [18]. When both catalysts are used simultaneously, the homologation activity is increased. For high concentrations of ruthenium (low θ-values) there is extensive formation of ethers. The main ether produced is the symmetrical ether formed from the starting alcohol and is obviously undesirable. Hydrocarbon formation is also important. In respect of the product composition the situation resembles that for high concentrations of cobalt ($\theta \approx 1$), but the homologation activity is highest when a small amount of ruthenium is present [19*].

The most interesting finding evident from Figs. 1 and 2 is that use of a θ-value between 0.80 and 0.85 allows the C_n alcohol to be homologated into the C_{n+1} and

Table 1

Co–Ru-catalyzed hydrocarbonylation of alcohols. Effect of catalyst composition on hydrocarbon formation[a]

Alcohol	Yield of hydrocarbons[b] (%)		
	$\theta = 0$	$\theta = 0.83$	$\theta = 1$
Ethanol	32	0–2	18
1-Propanol	29	1	13
2-Propanol	45	10	52
1-Butanol	6	1	14
2-Butanol	51	27	48
2-Methyl-1-propanol	9	5	5
2-Methyl-2-propanol	49	25[c]	23

[a] Conditions are indicated in text. θ is the [Co]/[Co + Ru] ratio in the catalyst (see text). [b] Based on converted alcohol. [c] Only 1% in the absence of the iodide promoter.

even the C_{n+2} alcohol. Hydrocarbon formation is considerably lowered [19*] (Table 1). Ethers are still present, but in several cases the mixed ether C_nOC_{n+1} is preferentially produced at the expense of the symmetrical ether C_nOC_n. For these θ-values there is undoubtedly a synergistic effect reflecting a dual action of the cocatalysts.

As stated in the introduction, alcohols other than methanol have usually been reported to undergo hydrocarbonylation with difficulty, and this is reflected in the previously reported homologation rates (Table 2). With the mixed Co/Ru system, however, the situation is very different: methanol is only twice as reactive as ethanol, and the rates for the other alcohols are of the same order of magnitude. As expected, the reactivity sequence tertiary > secondary > primary alcohol applies [20]. The agreement between V_g and V_1 value is fair. Our results show that our catalytic system is efficient in converting most alcohols into their next homologues but it is not recommended for methanol homologation which gives poor selectivity for ethanol formation.

Table 2

Hydrocarbonylation of alcohols. Rates and selectivity[a]

Alcohol ROH	Relative rates				$\Sigma^{b,e}$ (%)
	$V_g{}^b$	$V_g'{}^c$	$V_g''{}^d$	$V_1{}^b$	
Methanol	1.00	1.00	1.00	1.00	20
Ethanol	0.56	0.024	0.08	0.51	55
1-Propanol	0.38	–	–	0.35	60
2-Propanol	0.53	0.021	0.006	0.48	42
1-Butanol	0.35	–	–	0.25	40
2-Butanol	0.54	–	–·	0.52	57
2-Methyl-1-propanol	0.28	–	–	0.23	35
2-Methyl-2-propanol	0.94	2.41	–	0.80	80

[a] Rates expressed in moles of Syngas converted per mole of metal catalyst per h (V_g) or moles of alcohol converted/mole of metal catalyst per h (V_1). The methanol reaction is the reference. [b] This study $(\theta = 0.83, p$ 420 bar, T 200°C). [c] Bahrmann and Cornils [23]. Catalyst is $CoAc_2$/iodine. [d] Pretzer and Habib [21]. Catalyst is CoI_2/NaI. [e] Selectivity to $RCHO + RCH_2OH$.

Table 3

Hydrocarbonylation of alcohols. Effect of iodide promoters [a]

Alcohol ROH	Promoter	Conversion (%)	Yields [a] (%)		
			RCH_2OH	ROR	$ROCH_2R$
Ethanol [b]	none	4	2	1	1
($R = C_2H_5$)	I_2	60	21	7	15
	KI	31	23	1	7
	$KI + I_2$	38	20	3	10
1-Propanol [c]	I_2	41	23	11	?
($R = n-C_3H_7$)	KI	11	7	0.5	?
	$KI + I_2$	17	12	0.5	?
2-Propanol	none	1	0	0	0
($R = i-C_3H_7$)	I_2	58	22	12	9
	$KI + I_2$ [d]	6	2	3	0
1-Butanol	I_2	46	16	19	?
($R = n-C_4H_9$)	$KI + I_2$ [d]	15	10	1	?
2-Butanol	none	0	0	0	0
($R = CH_2CHC_2H_5$)	I_2	81	34	1	?
	$KI + I_2$ [d]	8	6	0.5	?
2-Methyl-2-propanol	none	85	76	0	0
($R = t-C_4H_9$)	I_2	99	44	0	0
	$KI + I_2$ [d]	99	79	0	0

[a] $\theta = 0.83$; T 200°C; t 2 h unless otherwise stated. Other conditions as indicated in text. Yields are based on substrate. [b] T 170°C; t 3 h. [c] T 180°C; t 2 h. [d] KI 0.9 mmol; I_2 0.16 mmol.

Table 4

Homologation of alcohols. Effect of pressure

Pressure (bar)	ROH	RCH_2OH [a]	RCH_2CH_2OH [a]
450	Ethanol [b]	13.6	0.4
	1-Propanol [c]	12.5	0.2
	1-Propanol [d]	8.1	0.1
	2-Propanol [c]	14.9	0.5
600	Ethanol [b]	7.6	0.6
	1-Propanol [c]	10.6	0.4
	1-Propanol [d]	8.4	0.2
	2-Propanol [c]	15.2	1.3
1000	Ethanol [b]	6.5	0.9
	1-Propanol [c]	9.0	0.6
	1-Propanol [d]	14.6	1.2
	2-Propanol [c]	16.4	2.2
2000	Ethanol [b]	5.5	1.7
	1-Propanol [c]	16.3	1.6

[a] Alcohols in mmol. Conditions as indicated in text unless otherwise stated. [b] I_2 as promoting agent, T 200°C; t 3 h. [c] I_2 as promoting agent, T 200°C; t 2 h. [d] $KI + I_2$ as promoting system (KI: 0.9 mmol, I_2: 0.16 mmol); T 180°C; t 2 h.

(ii) Effect of the promoter. The effect of the promoters in the hydrocarbonylation of alcohols has been investigated by Pretzer [21]. Under the conditions we used, the presence of an iodide is essential for the reaction. Except in the case of tertiary alcohols, there is negligible reaction in the absence of the promoter.

Iodine efficiently promotes the catalytic system as far as the selectivity towards the higher alcohol is concerned. Nevertheless, it also leads to the ether derived from the starting alcohol. Use of an ionic iodide also yields the higher alcohol, though in smaller amounts (Table 3). However, this observation holds only for primary alcohols and secondary alcohols give very poor results. For primary alcohols, the combination of iodine and an ionic iodide leads to an apparent lowering of the extent of conversion, but the selectivity for formation of the higher alcohol is improved, mainly because of the inhibition of ether formation; as shown in Table 3, very little of the symmetrical ether is formed when a mixture of I_2 and KI is used. In the case of methanol [22], this has been attributed to reduction of the acidity of the medium in the presence of an ionic iodide.

Effect of pressure

Pressure generally has a beneficial effect on the CO insertion and is an important parameter in the homologation of alcohols [23]. For all the alcohols studied, we found an optimal pressure range approximately between 400 and 550 bar (for temperatures of 170–200 ° C). The optimal pressure does not depend on the alcohol. Interestingly, an increase in pressure leads to a further homologation reaction (Table 4). The increase in the homologation activity is accompanied by a marked reduction of ether formation.

Discussion

Our results, considered along with those previously reported [5–7], raise several fundamental questions. Why does the Co–Ru–I catalytic system significantly promote the formation of the higher alcohol (Figs. 1, 2)? Why does it inhibit (or considerably reduce) the formation of hydrocarbons (Table 1)? Why are the results dependent on the promoter (Table 3)? What is the effect of pressure (Table 4)?

The general scheme for the formation of homologation products in hydrocarbonylation reactions is outlined in Scheme 1 in which the insertion of CO is assumed to be the first step [24].

The hydrocarbonylation of C_2–C_4 alcohols catalyzed by cobalt compounds differs from the methanol homologation in several ways, (inter alia): (i) the reaction rates are extremely low; (ii) the generation of alcohols is highly pressure dependent; (iii) a mixture of isomeric alcohols is produced wherever the starting alcohol can lead to an unsymmetrical olefin.

In connection with point (i), it is noteworthy that the homologation activity for higher alcohols is evident only above a certain threshold of the catalyst concentration (Table 5).

The results listed in Table 5 suggest a mechanistic scheme in which the key intermediate is an olefin formed by dehydration of the starting alcohol. The main argument for this is that the C_3 and C_4 alcohols give not only the expected homologation product but also the isomeric alcohol normally produced in the subsequent hydroformylation of the olefin (Table 6). Of course, this suggestion is
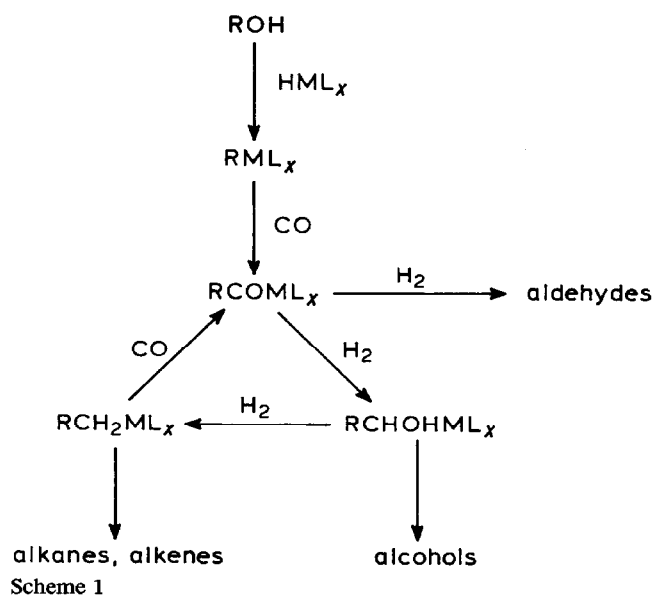
244

Scheme 1

Table 5

Co–Ru-catalyzed hydrocarbonylation of ethanol. Effect of catalyst concentration[a]

Co + Ru (mmol metal)	Conversion (%)	Products			
		$(C_2H_5)_2O$	C_3H_7OH	$C_2H_5OC_3H_7$	$(C_3H_7)_2O$
0.15	8	2.9	0	0	0
0.22	33	6.8	5.9	2.9	0.1
0.45	48	5.6	12.8	5.0	0.8
0.90	60	3.0	18.0	6.0	0.9

[a] $\theta = 0.83$; T 170 °C; t 3 h. Other conditions indicated in text. Products in mmol.

Table 6

Alcohols produced in the hydrocarbonylation of the lower alcohol

Starting alcohol	Intermediate olefin(s)	Alcohols produced	Distribution (%)
Ethanol	$CH_2=CH_2$	1-Propanol	
1-Propanol	$CH_2=CHCH_3$	1-Butanol	68
		2-Methyl-1-propanol	32
2-Propanol	$CH_2=CHCH_3$	1-Butanol	48
		2-Methyl-1-propanol	52
1-Butanol	$CH_2=CHCH_2CH_3$	1-Pentanol	78
		2-Methyl-1-butanol	22
2-Butanol	$CH_3CH=CHCH_3$	1-Pentanol	42 [a]
	$CH_2=CHCH_2CH_3$	2-Methyl-1-butanol	58 [a]
2-Methyl-1-Propanol	$CH_3C(CH_3)=CH_2$	3-Methyl-1-butanol	71
		2,2-Dimethyl-1-propanol	29
2-Methyl-2-propanol	$CH_3C(CH_3)=CH_2$	3-Methyl-1-butanol	90
		2,2-Dimethyl-1-propanol	10

[a] This distribution corresponds to the distribution of the intermediate olefin obtained by acid catalyzed dehydration of 2-butanol [49].

$$RCH_2CH_2OH \quad \underset{}{\overset{H^+}{\rightleftharpoons}} \quad (RCH_2CH_2)_2O$$

with downward arrow labeled $-H_2O$

$$RCH=CH_2 \quad \xrightarrow{H_2} \quad RCH_2CH_3$$

with downward arrow labeled $CO + H_2$

$$RCH_2CH_2CHO \quad + \quad RCH(CH_3)CHO$$

with downward arrows labeled H_2

$$RCH_2CH_2CH_2OH \quad\quad RCH(CH_3)CH_2OH$$

$$\Updownarrow$$

$$\text{ethers} \quad + \quad \text{mixed ethers}$$
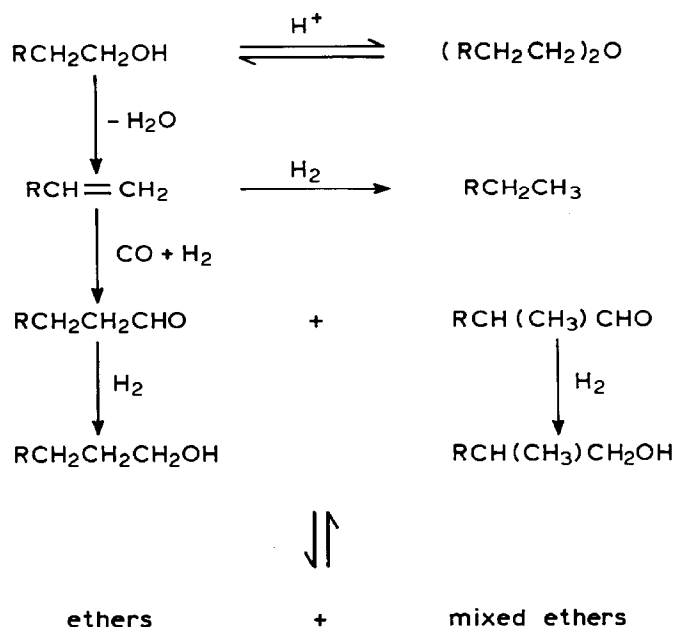
Scheme 2

not new, and has been proposed for cobalt catalysts in earlier [25,26] and recent years [21].

The routes to the products may be roughly depicted as shown in Scheme 2. However, the presence of olefins has never been detected in the gas phase in these reactions, except for minor amounts formed in the hydrocarbonylation of the four butanols. Clearly, if the olefin is formed, its absence under the conditions employed in this work suggest that the hydroformylation rate is higher then the rate of dehydration to give the transient olefin.

The typical mechanism of the transformation of alcohols into alkenes and ethers involves the protonated alcohol ROH_2^+, which is either dehydrated in an E_1 elimination process or undergoes an S_N1 substitution. Initially, however, there are no available protons in the medium. Under the action of Syngas, the cobalt catalyst gives rise to the strong acid $HCo(CO)_4$ which can protonate the alcohol. It should be noted that the cobalt catalyst, either alone or in conjunction with the Ru cocatalyst, is essential, since runs carried out with ethanol in the presence of iodine or with strong acids like H_2SO_4, H_3PO_4, HI, under the same conditions but in the absence of Co and Ru gave only diethyl ether.
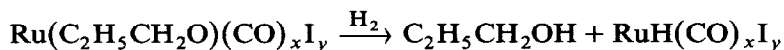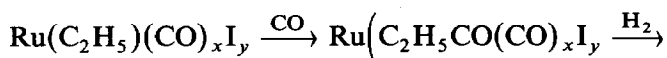
1. The possibility of an independent role of cobalt and ruthenium

We first consider the possibility that the higher alcohol is formed via a ruthenium or a cobalt complex species independently.
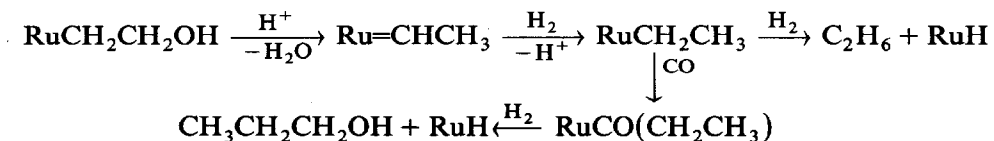
(*i*) In the case of ruthenium, an iodoruthenium carbonyl complex $RuR(CO)_xI_y$ could be involved. As shown elsewhere [27], this complex would liberate the olefin:

$$Ru(C_2H_5)(CO)_xI_y \rightarrow C_2H_4 + RuH(CO)_xI_y$$
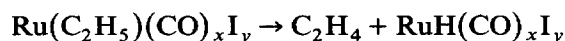
Direct chain growth involving this species has only been considered as a possibility for methyl and ethyl groups [28], e.g.:

$$Ru(C_2H_5)(CO)_xI_y \xrightarrow{CO} Ru\left(C_2H_5CO(CO)_xI_y \xrightarrow{H_2}\right.$$

$$Ru(C_2H_5CH_2O)(CO)_xI_y \xrightarrow{H_2} C_2H_5CH_2OH + RuH(CO)_xI_y$$

Warren et al. [29] have suggested that there may be a methylidene complex intermediate in acid medium that may facilitate conversion of the substrate into alkyl iodide or activate it in other ways for its addition to a metal center. A possible representation of the process is:

$$RuCH_2CH_2OH \xrightarrow[-H_2O]{H^+} Ru{=}CHCH_3 \xrightarrow[-H^+]{H_2} RuCH_2CH_3 \xrightarrow{H_2} C_2H_6 + RuH$$
$$\downarrow CO$$
$$CH_3CH_2CH_2OH + RuH \xleftarrow{H_2} RuCO(CH_2CH_3)$$

(*ii*) In the case of the cobalt system, there is the possibility of an alkylcobalt species $RCo(CO)_4$ formed by reaction of the alcohol or the corresponding alkyl iodide with $HCo(CO)_4$ as in the methanol homologation, since it is known that the high acidity of $HCo(CO)_4$ is useful in facilitating the nucleophilic attack on the alcohol and in displacing the alkyl iodide equilibrium [30]:

$$C_2H_5OH \xrightarrow[-H_2O]{HI} C_2H_5I \xrightarrow[-HI]{HCo(CO)_4} C_2H_5Co(CO)_4$$
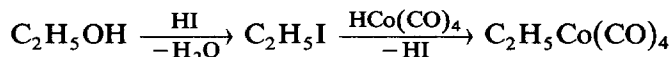
However, higher alcohols react more slowly than methanol with $HCo(CO)_4$ to form an alkyl–metal bond.

If there is an olefinic intermediate, this could be generated either from $Ru(R)(CO)_xI_y$ or by decomposition of $Co(R)(CO)_4$.

We tentatively propose the mechanistic scheme shown in Scheme 3 for the Co–Ru-catalyzed homologation of higher alcohols based on the assumption that the Co and Ru act independently (Scheme 3).

This Scheme shows two routes leading to the aldehyde via the olefin or the acyl-metal species. The rate-limiting step in the olefin formation may be the formation of the alkyl–metal bond, a suggestion analogous to those made by Hunf [31] and Françoisse [32]. Scheme 3 does not show how this bond is formed; there are several possible routes, as described by Bahrmann and Cornils in the case of methanol [33].

In the case of the olefinic pathway, the acylmetal complex is also assumed to be formed in the hydroformylation mechanism [34]. The cleavage of acylcobalt carbonyls has been discussed recently [35–37]. It may involve attack by molecular hydrogen or by $HCo(CO)_4$, the first possibility being the more likely [35,36], while a radical mechanism was proposed for the reaction with $HCo(CO)_4$ [37].

## 2. Synergistic behavior of the Co and Ru catalysts

Since the addition of small amounts of ruthenium considerably promotes the production of alcohols, an independent action of the two is doubtful. Recent studies have shown that ruthenium catalysts may have important effects in reactions

$$I_2 + H_2 \underset{}{\overset{H_2O}{\rightleftharpoons}} 2HI$$
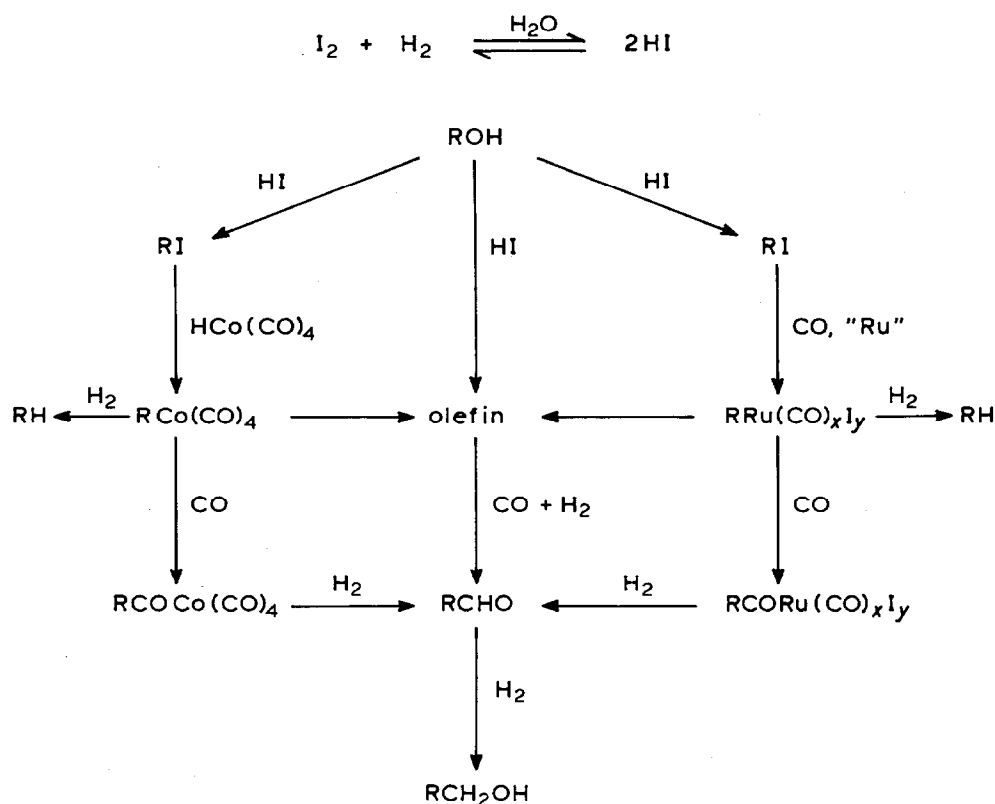
Scheme 3

involving organocobalt compounds, and it has been proposed that a ruthenium hydride is responsible for the enhancement of the rate of reduction of Co^{2+} to $Co(CO)_4^-$ [13,38]. In the case of hydroformylation, Hidai suggested attack of ruthenium hydrides such as $[HRu_3(CO)_{11}]^-$ on the acylcobalt complex [9]. He also recently found evidence for a dinuclear reductive elimination of aldehydes from acylcobalt carbonyls via a complex reaction with $HRu(CO)_4^-$ [39]. It therefore seems that ruthenium is a true cocatalyst in the cobalt-catalyzed hydroformylation.

This can also account for the great reduction, and in some cases, the complete suppression, of hydrocarbon formation, presumably as a result of considerable enhancement of the rate of hydroformylation relative to that of hydrogenation, as discussed above. With the systems Co/I_2 and Ru/I_2 there is also some homologation activity [40*], though much lower, suggesting that there is still formation of the olefin. However, with such catalytic systems, the hydroformylation reaction is less favoured and, consequently, in the hydrocarbonylation process large amounts of hydrogenation products are formed (Table 1), especially in the presence of ruthenium [41]. With the bimetallic Co/Ru catalytic system, the production of hydrocarbons is increased with increasing concentrations of Ru (e.g. for lower θ-values), and these are possibly generated according to [28]:

$$RuR(CO)_xI_y + H_2 \rightarrow RuH(CO)_xI_y + RH$$
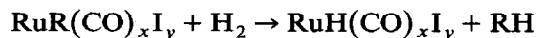
This may be one of the reasons for the existence of an optimal θ-value.

3. Role of the iodide promoter

As shown in Table 3, the nature of the promoter plays an important role in the reaction. The effect of the promoter was examined by Pretzer [21] for the hydrocarbonylation of several alcohols with iodine-promoted cobalt catalysts, and his main conclusions may be summarized as follows:

(i) For alcohols that are easily dehydrated an E_1 elimination pathway leading to the olefin should be favoured. t-Butanol is a good example, since homologation proceeds in the absence of promoter; indeed, the presence of iodine decreases the yield of C_5 alcohols by promoting side reactions (mainly hydrocarbon formation).

(ii) For all other alcohols, hydrocarbonylation involving a nucleophilic attack by I^- on the protonated alcohol to give an alkyl iodide (S_N2 process) should be favoured.

Of course, both pathways might operate simultaneously.

It is clear that with cobalt catalysts, primary alcohols will follow the S_N2 mechanism, particularly when there is a high concentration of a strong nucleophile. The I^- anion is, of course, a considerably stronger nucleophile than I_2. For those systems promoted by free iodine, the iodide is probably present as HI, which facilitates the dehydration of the alcohol when associated with the cobalt catalyst.

In contrast to Pretzer's suggestions, we found in the present study that the introduction of the ruthenium catalyst seems to minimize the S_N2 process even for primary alcohols, except perhaps for Co/Ru catalytic systems promoted by I^-. This suggestion is only speculative at present, but is supported by the fact that 1-propanol gives a 2/1 ratio (n-butanol/i-butanol) regardless of the promoting agent used (I_2, CH_3I, KI or mixtures of them). If a pure S_N2 process operated with KI, then 1-propanol should afford only 1-butanol. This may be partially correct, since in the homologation of 2-propanol the butanols ratio (n/i) is approximatively 1/1 with iodine as promoter but changes to 1/4 when KI is used [6].

4. Role of pressure

Pressure is an important parameter in the Co–Ru-catalyzed homologation of higher alcohols and may be more important than in the cobalt-catalyzed homologation of methanol [2,42]. The large pressure dependence observed suggests the possibility of catalytic transformations as integral parts of the catalytic process. At low pressures (< 200 bar), ether formation via a S_N1 process is the dominant reaction, while neither the E_1 nor the S_N2 mechanism can operate since $HCo(CO)_4$ is not stable. An increase in the pressure improves the stability of the catalyst, ether formation is hindered, and the homologation process can take place concurrently. However, there should be no change in the acidity of the medium, since mixed ethers are formed in appreciable amounts. One can only say that the overall homologation rate is higher than the etherification rate.

Comparison with other S_N1, S_N2, E_1 processes investigated at high pressure reveals that these processes are usually characterized by negative volumes of activation $\Delta V^\ddagger$ [43] and, so are accelerated by pressure. The S_N1 and E_1 mechanisms, however, involve the formation of carbenium ions, and hence electrostriction, affecting the magnitude of $\Delta V^\ddagger$. The high polarity of alcohols should reduce the negative value of $\Delta V^\ddagger$, since the volume of activation of polar reactions increases with increasing solvent polarity (i.e. $\Delta V^\ddagger$ becomes less negative) [44].

The situation, however, it is not straightforward for homologation reactions, since catalytic species which intervene in the transition state are involved. One of these

species is probably $HRu_3(CO)_{11}^-$ [39,45], which may undergo a fragmentation with CO to produce the more reactive mononuclear hydride $HRu(CO)_4^-$ [45,46]. The reaction occurs under high CO pressure and is independent of the structure of the substrate. This may account for the fact that the optimal pressure is the same for the homologation of all the alcohols, and suggests the formation of a common catalytic species that does not include the alkyl part of the substrate. The existence of the optimum does not necessarily mean that the catalytic activity diminishes at higher pressures, simply that the higher aldehydes and alcohols undergo reactions leading to products containing larger groups [47].

5. Formation of by-products

Typical by-products formed along with alcohols include hydrocarbons, ethers, and esters. In Scheme 3 it is suggested that the hydrocarbons may be produced in various ways e.g. by hydrogenation of the ruthenium iodocarbonyl species, of the alkyl cobalt carbonyl species, and of the olefin. What is remarkable is that despite the presence of the powerful hydrogenation Ru catalyst, the hydrocarbon yield drops for $\theta \simeq 0.83$. We suggest that kinetic factors are responsible for this.

Formation of ethers can proceed via a nucleophilic attack of alcohols or water on alkyl metal complexes. Primary alcohols readily undergo etherification, whereas secondary alcohols give only small amounts of ethers. Clearly, a complex adjustment of the experimental conditions is required to direct the dehydration toward the olefin.

Normally, formation of acetates would not be expected, and we suspect that the initial cobalt catalyst is responsible for their production. The catalyst used was cobalt acetate tetrahydrate, and the concentration of acetates for each alcohol corresponds fairly well to the acetate part of the cobalt catalyst. Replacing cobalt acetate by $Co_2(CO)_8$ does, as expected, suppress the formation of alkyl acetates.

Formates are present in very small amounts and only in the homologation of ethanol and 1-propanol. Their formation can be accounted for in terms of the scheme depicted for methanol [48].

The other esters are principally those resulting from the esterification of the acid corresponding to the C_{n+1} alcohol. Their formation may be simply accounted for in terms of Scheme 3 by alkoxycarbonylation of the intermediate olefin:

$$C_nH_{2n} + CO + ROH \rightarrow C_nH_{2n+1}COOR$$

Aldehydes are also present, mostly in low concentrations, except in the case of 1-propanol where, surprisingly, 1-butanal is produced in significant yield and is not completely hydrogenated under our conditions [6].

Finally, in the hydrocarbonylation of butanols, symmetrical ketones are formed, e.g. 5-nonanone from 1-butanol. Their formation can be formulated as a reaction between the acylcobalt compound and the alkylcobalt complex, as was shown to be the case in hydroformylation reactions [47].

Conclusion

This study has shown that the mechanism of the homologation of higher alcohols in the presence of mixed cobalt–ruthenium catalysts is different from that for homologation of methanol. Though a S_N2 mechanism may contribute in some

cases, there is evidence that except for methanol every alcohol is partially or fully homologated via an olefinic intermediate. The role of ruthenium is probably complex, but may be rationalized in terms of the formation of a ruthenium carbonyl hydride that then reacts with the acylcobalt complex. The optimal composition of the Co–Ru–I catalytic system involves a delicate balance between antagonistic (formation of hydrocarbons) and synergistic effects (hydroformylation) of the Ru [9,39].

The selectivity towards the higher alcohols must still be improved. If the presence of an olefinic intermediate is confirmed, this study could have important consequences in that reactions involving an olefin, a second reacting molecule, and Syngas might be possible starting from the alcohol. This was observed in homologation of the alkoxy moiety of esters [10].

Acknowledgements

References

1 I. Wender, R. Levine and M. Milton, J. Am. Chem. Soc., 71 (1949) 4160.
2 However, a 100% conversion of methanol with nearly 90% selectivity to ethanol was claimed for homologation in chelating solvents. G. Jenner and P. Andrianary, J. Catal., 88 (1984) 535.
3 A. Sugier and E. Freund (to Institut Français du Pétrole), Fr. 7835870 (1978).
4 See literature cited references 5–7.
5 G. Jenner and P. Andrianary, J. Catal., 103 (1987) 37.
6 P. Andrianary, G. Jenner, S. Libs and G. Teller, J. Mol. Catal., 39 (1987) 93.
7 P. Andrianary and G. Jenner, J. Organomet. Chem., 322 (1987) 89.
8 H. Kheradmand, G. Jenner, A. Kiennemann and A. Deluzarche, Chem. Lett., (1982) 395.
9 M. Hidai, A. Fukuoka, Y. Koyasu and Y. Uchida, J. Chem. Soc., Chem. Commun., (1984) 516.
10 G. Jenner and P. Andrianary, J. Organomet. Chem., 307 (1986) 263.
11 G. Jenner and G. Bitsi, Appl. Catal., 32 (1987) 293.
12 G.N. Butter (to Commercial Solvents), US 3 285 948 (1966).
13 J. Gautier-Lafaye and R. Perron (to Rhône-Poulenc), Eur. Pat. 22038 (1981).
14 W.R. Pretzer, J.E. Bozik and T.P. Kobylinski (to Gulf) Eur. Pat. Appl. 55887 (1982).
15 G. Doyle, J. Mol. Catal., 18 (1983) 251.
16 K. Watanabe, K. Kudo and N. Sugita, Bull. Chem. Soc. Jpn, 58 (1985) 2029.
17 J. Gautier-Lafaye, R. Perron and Y. Colleuille, J. Mol. Catal., 17 (1982) 339.
18 (a) G. Braca, G. Sbrana, G. Valentini, G.P. Andrich and G. Gregorio, Fundamental Research in Homogeneous Catalysis, Vol. 3, Plenum, New-York, 1979, p. 221; (b) G. Braca, A.M. Raspolli and G. Sbrana, ACS Symp. Ser., 328 (1987) 220.
19 The nature of the ruthenium and the cobalt compound is not critical unless heterogeneous catalysis is involved. For example, in ethanol homologation, a combination of $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ gives results quite similar to those obtained with the mixture of $Co(OAc)_2$ and $Ru(acac)_3$. In contrast, use of the system $Co_2(CO)_8/RuO_2$ lowers the yield of propanol by 60% owing to the insolubility of RuO_2.
20 I. Wender and P. Pino, Organic Synthesis via Metal Carbonyls, Vol. 2, Wiley, New York, 1977, p. 18.
21 W.R. Pretzer and M. Habib, in R.G. Herman (Ed.), Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals, Plenum Press, New-York, 1984, p. 261.
22 M. Röper and H. Loevenich, J. Organomet. Chem., 255 (1983) 95.
23 H. Bahrmann and B. Cornils, in J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer Verlag, Berlin, 1980, p. 226.
24 W. Keim, Catalysis in C_1 Chemistry, D. Reidel, Dordrecht, 1983, p. 21.

25 G.R. Burns, J. Am. Chem. Soc., 77 (1955) 6615.

26 K.H. Ziesecke, Brennst. Chem., 33 (1952) 385.

27 G. Jenner, H. Kheradmand, A. Kiennemann and A. Deluzarche, J. Mol. Catal., 18 (1983) 61.

28 G. Braca, L. Paladini, G. Sbrana, G. Valentini, G. Andrich and G. Gregorio, Ind. Eng. Chem. Prod. Res. Dev., 20 (1981) 115.

29 B.K. Warren and B.D. Dombek, J. Catal., 79 (1983) 334.

30 V. Galamb and G. Palyi, Coordin. Chem. Rev., 59 (1984) 203.

31 G.H. Hunf, Ph.D, R.W.T.H., Aachen (RFA), 1978.

32 P.B. Françoisse and F.C. Thyrion, Ind. Eng. Chem. Prod. Res. Dev., 22 (1983) 542.

33 H. Bahrmann and B. Cornils, Chem. Ztg., 106 (1982) 249.

34 R.F. Heck and D.S. Breslow, J. Am. Chem. Soc., 83 (1961) 4024.

35 J.T. Martin and M.C. Baird, Organometallics, 3 (1984) 197.

36 M.F. Mirbach, J. Organomet. Chem., 265 (1984) 205.

37 J. Azran and M. Orchin, Organometallics, 3 (1984) 197.

38 M. Leconte and R. Perron, Atelier Metal-Metal, Société Chimique de France, Strasbourg, 1984.

39 Y. Koyasu, A. Fukuoka, Y. Uchida and M. Hidai, Chem. Lett., (1985) 1083.

40 Indeed ruthenium catalysts have been reported to hydroformylate olefins: (a) H.F. Schultz and F. Bellstedt, Ind. Eng. Chem. Prod. Res. Dev., 12 (1973) 176; (b) R.A. Sanchez-Delgado, J.S. Bradley and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1976) 399.

41 M. Bianchi, G. Menchi, P. Frediani, U. Matteoli and F. Piacenti, J. Organomet. Chem., 247 (1983) 89.

42 P. Andrianary, G. Jenner and A. Kiennemann, J. Organomet. Chem., 252 (1983) 209.

43 N.S. Isaacs, Liquid Phase High Pressure Chemistry, Wiley, New-York, 1981.

44 H. Kelm and D.A. Palmer, High Pressure Chemistry, D. Reidel, Dordrecht, 1978, p. 300.

45 (a) B.D. Dombek, J. Organomet. Chem., 250 (1983) 467; (b) B.D. Dombek, Organometallics, 4 (1985) 1707.

46 M. Tanaka, T. Sakakura, T. Hayashi and T. Kobayashi, Chem. Lett., (1986) 89.

47 B. Cornils, Ref. 23, p. 141.

48 G.S. Koermer and W.E. Slinkard, Ind. Eng. Chem. Prod. Res. Dev., 17 (1978) 231.

49 R.J. Arhart and J.C. Martin, J. Am. Chem. Soc., 94 (1972) 5003.