REDUCTIVE CARBONYLATION OF CARBOXYLIC ESTERS IN THE PRESENCE OF HOMOGENEOUS RUTHENIUM-COBALT SYSTEMS. HOMOLOGATION OF THE ALKOXY MOIETY

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Summary

Homogeneous Co-Ru systems in the presence of an iodide promotor can catalyse homologation of the alkoxy moiety of carboxylic esters. For low molecular weight esters, the ruthenium has a synergistic effect. The mechanism is thought to parallel that of the mechanism generally applying to the homologation of alcohols, and is believed to involve at least in part an olefinic intermediate originating from the alkyl moiety and undergoing hydroformylation into the higher alcohol. Subsequent esterification produces the expected ester. The best yields of the higher ester are obtained when elemental iodine is used along with an ionic iodide.

Introduction

Homologation reactions are valuable processes, for they involve conversion of a C_n substrate into the next higher C_{n+1} compound via hydrocarbonylation. The preferred metal catalyst is cobalt, whose compounds react readily with syngas to give the strong acid $HCo(CO)_4$ which subsequently undergoes decarbonylation to $HCo(CO)_3$, the active catalyst [1].

The cobalt catalyst has both carbonylation and hydrogenation activity. In recent years, however, several authors have used cocatalysts either to improve the hydrogenation properties of the catalytic system [2–4] or to convert the substrate into a compound more suitable for reacting with syngas to afford the homologation product. The last category includes the hydrocarbonylation reactions of methyl esters, which are converted into ethyl esters. The reaction has been investigated by several authors [5–7], who showed that the homologation occurs via esterification of the corresponding carboxylic acid and ethanol, which is the actual homologation product. The mechanism initially proposed by Braca [5] for ruthenium catalysts was extended to the case of a mixed catalytic system consisting of a cobalt compound, a ruthenium compound, and an ionic iodide [8].

With this mixed catalyst system only methyl esters gave satisfactory results [9]; attempts to homologate other alkyl groups under the conditions employed for methyl esters were unconclusive. A patent [10] reported the preparation of n-propyl, n-butyl, and isoamyl acetate from the corresponding lower acetate in the presence of high concentration of cobalt catalysts with or without iodine. Another report was concerned with the homologation of isopropyl and t-butyl acetate [11]; in this case the t-butyl acetate gave good results (homologation product: isoamyl acetate) but, the hydrocarbonylation of isopropylacetate gave a large number of side products (80 to 99%). It is noteworthy that Braca et al. reported some reactions occurring in the presence of syngas with formic and higher molecular weight carboxylic acid esters catalyzed by ruthenium carbonyl iodide [12], but except for methyl formate, the homologation products were produced only in low yields; interestingly, Braca et al. showed that under these conditions both the acyl and the alkyl moiety of the ester molecule may undergo homologation. More recently Lütgendorf et al. studied the reductive carbonylation of esters with the same catalytic system [16]. They found that the dominant process was the carbonylation of the alkoxy moiety rather than the homologation of the acetyl or alkoxy moieties.

The scarcity and, often, a lack of conviction in the results prompted us to re-investigate these reactions in the presence of the cobalt-ruthenium-iodine system which was found to be particularly efficient for the homologation of alcohols [13].

Experimental

The experiments were carried out in an electrically heated 15 ml-titanium stainless steel rocking autoclave. The catalysts, promoters and ester were introduced under an argon stream. Then the appropriate syngas pressure was applied and the autoclave heated and shaken. At the end of the run, the autoclave was cooled, slowly vented, and opened. An internal standard (diglyme) was added to the homogeneous mixture which was analyzed by GLC. The analyses were performed on a Hewlett–Packard 5700 chromatograph with a thermal conductivity detector. A Porapak R column was used (Inox, 4 m, $\varnothing$ 1/8″, 80–100 mesh, 50–240°C, 4°C/min). Gas samples were analyzed by GC (Chromosorb 101, 4 m, $\varnothing$ 1/8″, 65–230°C, 4°C/min) and molar quantities determined from experimental calibration curves.

Symbolism: HC: hydrocarbons; C: ester conversion; alcohols are designated by ROH, acids by RCO_2H, esters by RCO_2R'.

Results

We thought it likely that the hydrocarbonylation reaction of methyl esters parallels the corresponding methanol homologation, since in both cases the actual homologation product is ethanol. We thus thought that if we are able to generate the higher alcohol from the lower alkyl moiety of the considered ester, then the homologation could be achieved.

In a previous study it was shown that higher alcohols can also be homologated under special conditions; for example ethanol to propanol [13]. The catalytic system was a Co-Ru-I combination, but its concentration had to be much higher than in the corresponding methanol reaction in order to produce the presumed synergistic

effect. To rationalize the results, we proposed a mechanism in which the key step would be the dehydration of the starting alcohol into the alkene followed by its hydroformylation, the dehydration being greatly facilitated by the presence of both ruthenium and iodine.

In this respect, we note that metal hydride compounds (Ru, Co, Ir...) are excellent catalysts for conversion of the esters to acids (eq. 1). It is reasonable to

$$R-C{\overset{O}{\underset{OR'}{\Big<}}} \quad \xrightarrow{\quad LnMH \quad} \quad RCOOH \; + \; R'MLn \quad\quad (1)$$

assume that, if the alkene corresponding to R' could be generated, then it might be possible to homologate the alkoxy moiety of any ester RCOOR' to give the next higher ester $RCOOCH_2R'$. Thus using the same conditions as those employed in the homologation of ethanol and higher alcohols (the parameters were not varied) we examined the hydrocarbonylation of several esters. Conditions used throughout were: Ester: 5 ml; cobalt(II) acetate, tetrahydrate (designated by Co): 0.75 mmol; ruthenium(III) acetylacetonate (designated by Ru): 0.15 mmol; Iodine or lithium iodide (calculated as I): 3.00 mmol; CO pressure: 14 MPa; H_2 pressure: 28 MPa; temperature: 200°C; reaction time: 2 h.

Four linear ethyl esters (formate to butyrate), the two propyl acetates, and t-butyl acetate were subjected to hydrocarbonylation [14]. For each ester four to six runs were carried out: two with the Co catalyst alone (0.75 mmol) with either I_2 or LiI, two with the only Ru catalyst (0.15 mmol) and two with the mixed Co-Ru catalytic system associated with either free iodine or LiI as promoters. Tables 1 and 2 list the results.

It should first be noted that the number of products differs greatly from one ester to another. For example, ethyl formate, ethyl acetate, and propyl acetates give a wide spectrum of compounds; all major products could be easily identified. However the mass balance was not always complete, especially in some Ru/I_2 experiments (the additional products observed by Braca [12] are not shown in the Tables) and in the hydrocarbonylation of t-butyl acetate.

Some features are as follows:

(i) The ester RCOOR' gives the corresponding acid RCOOH (see eq. 1). This does not appear in the ethyl formate reaction, since HCOOH cannot be detected by our GC system. The amount of acid is highest with catalytic systems containing Co and I_2, and much lower in the presence of Ru alone or when LiI is used as promoter.

In some cases involving the Co-Ru-I_2 system (but not when LiI is used as promoter), there is also an apparent homologation reaction of the acid RCOOH into RCH_2COOH (hydrocarbonylation of HCO_2Et, $MeCO_2Et$). Though the direct homologation of carboxylic acids has been reported with ruthenium catalysts [15], we have confirmed that under our conditions acids are not directly homologated. A closer examination of the results, however, shows that the acid does not come from RCO_2H, but from the alkyl group R' (thus in the reaction involving ethyl butyrate, no pentanoic acid is produced, but propionic acid, with propyl acetates, n-and i-butyric acids etc., are formed) probably via reaction 2.

$$RCOOR' + CO + H_2O \rightarrow RCOOH + R'COOH \quad\quad (2)$$

TABLE 1. HYDROCARBONYLATION OF ETHYL ESTERS [a]

Ethyl formate (HCO_2Et)

Catalyst	C(%)	EtOH	PrOH	EtCHO	$MeCO_2H$	$MeCO_2Et$	$MeCO_2Pr$	HCO_2Pr	HCO_2Bu	$EtCO_2Et$	HC[c]
$Co\text{-}I_2$	40	2.28	0	0.74	0.53	1.70	0	0.16	0	1.00	17.9
$Ru\text{-}I_2$	54	3.69	0.37	0.70	2.33	1.51	1.40	2.61	0.04	8.90	11.8
$Co + Ru\text{-}I_2$	72	5.76	1.05	0.36	0.77	1.93	0.32	3.34	0.16	4.94	24.7
$Co\text{-}LiI$	20	9.24	0.18	2.09	1.27	3.58	0	0.60	0.05	1.31	[c]
$Ru\text{-}LiI$	25	10.46	0.43	0	0	1.75	0	1.17	0.05	1.09	[c]
$Co + Ru\text{-}LiI$	46	8.11	1.75	0.36	0	1.30	0	4.90	0.23	2.16	[c]

Ethyl acetate ($MeCO_2Et$)

Catalyst	C(%)	EtOH	PrOH	$MeCO_2H$	$EtCO_2H$	$MeCO_2Pr$	$MeCO_2Bu$	$EtCO_2Et$	$EtCO_2Pr$	HC[c]
$Co\text{-}I_2$	69	0	0	23.20	2.24	2.04	0.30	2.93	0.71	3.1
$Ru\text{-}I_2$	38	0	0	6.28	0.97	1.93	0.80	2.45	0	7.2
$Co + Ru\text{-}I_2$	76	0.78	0.27	24.43	1.84	8.99	0.80	[b]	0.38	7.2
$Co\text{-}LiI$	21	6.07	2.35	11.75	0	2.45	0.31	[b]	0.53	[c]
$Ru\text{-}LiI$	15	2.52	0.35	5.82	0	2.22	0.40	2.62	0	[c]
$Co + Ru\text{-}LiI$	40	5.02	2.48	9.18	0.97	9.61	0.30	[b]	0.29	[c]

Ethyl propionate ($EtCO_2Et$)

Catalyst	C(%)	EtOH	PrOH	$EtCO_2H$	$PrCO_2H$	$EtCO_2Pr$	$EtCO_2Bu$
$Co\text{-}I_2$	65	0	0	20.03	1.48		0
$Ru\text{-}I_2$	45	0	0	14.88	4.37		0
$Co + Ru\text{-}I$	81	0	0	34.93	5.12		0.96
$Co + Ru\text{-}LiI$	35	4.56	2.23	4.95	7.41		0.43

Ethyl butyrate ($PrCO_2Et$)

Catalyst	C(%)	EtOH	PrOH	$PrCO_2H$	$EtCO_2H$	$PrCO_2Pr$	HC[c]
$Co\text{-}I_2$	78	0	0	21.57	1.03	3.63	1.5
$Ru\text{-}I_2$	57	0	0	8.26	3.74	2.93	1.1
$Co + Ru\text{-}I_2$	80	0	0	22.89	2.11	4.74	0.8
$Co\text{-}LiI$	25	3.54	2.62	4.98	0	3.17	[c]
$Ru\text{-}LiI$	20	2.45	1.18	1.45	0	2.85	[c]
$Co + Ru\text{-}LiI$	25	3.09	3.27	3.49	0	6.28	[c]

[a] Products in mmol. In some runs, there are additional minor (unidentified) products. [b] Not calculated (overlapping of GC peaks). [c] Ethane + propane.

TABLE 2

HYDROCARBONYLATION OF PROPYL ACETATES AND t-BUTYL ACETATE [a]

n-Propyl acetate ($MeCO_2Pr$)

Catalyst	C(%)	PrOH	BuOH	iBuOH	$MeCO_2H$	$PrCO_2H$	$i-PrCO_2H$	$MeCO_2Bu$	$MeCO_2$-i-Bu	C_5esters [b]	$PrCO_2Pr$	HC [e]
Co-I$_2$	74	0.40	c	(c)	21.75	1.90	0.57	1.21	1.22	0	1.28	4.3
Ru-I$_2$	36	0	0	0	7.65	0	0	2.49	0.47	0	2.83	2.2
Co+Ru-I$_2$	76	0.33	c	(c)	25.72	1.03	0.23	2.67	2.20	0.19	0.84	1.3
Co+Ru-LiI	32	3.88	1.92	0.66	3.42	0	0	3.22	2.07	0.08	0.23	c

i-Propyl acetate ($MeCO_2$iPr)

Catalyst	C(%)	i-PrOH	BuOH	i-BuOH	$MeCO_2H$	$PrCO_2H$	$i-PrCO_2H$	$MeCO_2Bu$	$MeCO_2$-i-Bu	C_5esters [b]	HC [e]
Co-I$_2$	95	0.67	c	c	30.28	0.53	3.33	0.31	2.67	0	1.3
Ru-I$_2$	c	0	0	0	(c)	0	1.01	1.53	2.17	0	1.3
Co+Ru-I$_2$	97	0	c	c	32.97	0.91	3.68	2.92	6.00	0.38	1.3
Co-LiI	c	5.67	0	0.85	c	0	0	1.96	1.97	0	c
Ru-LiI	c	4.65	0	0.28	c	0	0	1.10	0.81	0	c
Co+Ru-LiI	c	4.65	0	0.47	0.47	0	0	1.65	1.92	0	c

t-Butyl acetate ($MeCO_2$tBu)

Catalyst	C(%)	i-AmOH	t-AmOH [d]	$MeCO_2H$	$MeCO_2$-i-Am	$MeCO_2$-t-Am [d]	HC [f]
Co-I$_2$	100	5.45	0	30.55	0.48	0.33	3.7
Ru-I$_2$	100	5.39	0	17.28	0.26	0	14.1
Co+Ru-I$_2$	100	9.51	0.12	33.90	6.23	1.35	c
Co+Ru-LiI	90	1.27	0	12.15	12.48	1.34	c
Co-Ru	99	3.92	0.55	9.78	22.72	2.15	c

[a] Products in mmol. Additional products in the t-butyl acetate runs. [b] n-Amyl and i-amyl acetate. [c] Not calculated (overlapping of GC peaks). [d] Neopentanol (tAmOH), neopentylacetate ($MeCO_2$tAm). [e] Propane+butanes. [f] Isobutane.

TABLE 3

FORMATION OF HIGHER ESTERS IN THE HYDROCARBONYLATION OF FORMATES AND ACETATES [a]

Starting ester	Molar ratio		
	$RCOOCH_2R'$	:	$RCOO(CH_2)_2R'$
Ethyl formate	95	:	5
Ethyl acetate	92–96	:	4–8
Propyl acetate	96	:	4
i-Propyl acetate	96	:	4
Butyl acetate	100	:	0

[a] Catalytic system: $Co + Ru/I_2$ or $Co + Ru/LiI$.

(ii) The alkyl moiety of the ester gives rise to the corresponding alcohol R'OH and to the next higher alcohol $R'CH_2OH$, especially when LiI is used as promoter.

(iii) In each case the alkyl moiety R' is homologated into the next alkyl group, which in turn can undergo a further homologation, but the reaction is restricted to the ethyl and propyl groups (Table 3), in apparent accordance with a Schulz–Flory distribution.

(iv) Conversion of the ester is maximum with $Co-I_2$ and $Co-Ru-I_2$ catalytic systems. This arises mainly from disproportionation of the ester.

(v) The $Ru-I_2$ system catalyses homologation of the acyl as well as of the alkoxy moiety, though much less effectively than the $Ru-Co-I_2$ system. These results are in agreement with those of other recent studies [12,16].

(vi) The effects of added ruthenium catalyst and the iodide promoter are puzzling, since for low molecular weight esters there is a synergistic effect, while for higher esters, (R or R' ≡ n-propyl, n- and i-butyl) use of the Co-Ru combination does not improve the homologation, and can even be detrimental for the homologation of the alkoxy moiety (not, however in the case of t-butyl acetate) (Table 4).

(vii) Except in the hydrocarbonylation of ethyl formate and t-butyl acetate, the amount of hydrocarbons produced in the reaction is low. With LiI as promoter, the yield is very low.

(viii) If it is assumed that the ester $RCOOCH_2R'$ is formed by esterification of RCOOH with the higher alcohol $R'CH_2OH$, in all reactions involving LiI the

TABLE 4

EFFECT OF THE CATALYTIC SYSTEM ON THE FORMATION OF RCO_2CH_2R'

Starting ester	$Co/I_2 + Ru/I_2$ [a]	$Co + Ru/I_2$	$Co/LiI + Ru/LiI$ [a]	$Co + Ru/LiI$
Ethyl formate	2.81	3.50	1.87	5.13
Ethyl acetate	5.07	9.79	5.38	9.91
Ethyl propionate	5.85	6.08	–	–
Ethyl butyrate	6.56	5.74	6.02	6.28
n-Propyl acetate	5.39	5.06	–	–
i-Propyl acetate	6.68	9.30	5.84	3.57
n-Butyl acetate	7.22	5.77	–	–
i-Butyl acetate	3.07	1.48	–	–
t-Butyl acetate	1.07	7.58	–	–

[a] Sum of the amount $RCO_2CH_2R' + RCO_2(CH_2)_2R'$ (in mmol) obtained in the separate runs with Co and Ru respectively.

TABLE 5

PROMOTING EFFECT OF THE $(LiI + I_2)$ SYSTEM ON THE FORMATION OF RCO_2CH_2R' [a]

Starting ester	Catalytic system	
	$Co + Ru/LiI$ [a]	$Co + Ru/LiI + I_2$ [a,b]
Ethyl formate	4.90	6.13
Ethyl acetate	9.91	14.98
Ethyl butyrate	6.28	8.61
Propyl acetate	5.29	10.15
i-Propyl acetate	3.57	6.50
Butyl acetate	5.12	6.31
i-Butyl acetate	0.22	0.67

[a] Co (0.75 mmol); Ru (0.15 mmol); LiI (3.00 mmol). [b] I_2 (0.37 mmol).

liberated acid is present only in low proportion, and the yield of the ester is consequently reduced. Thus if the concentration of the acid is increased (for example by the addition of a small quantity of iodine in conjunction with LiI), then the yield of $RCOOCH_2R'$ is improved, and Table 5 shows that this is the case:
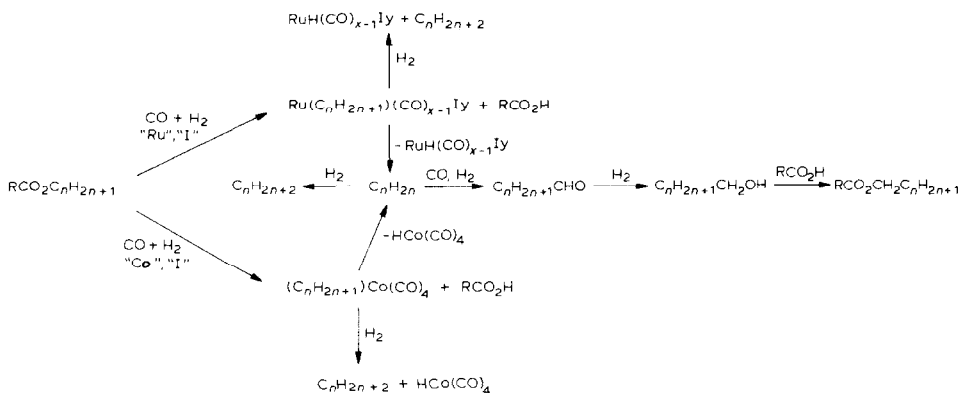
$$RCOOR' + HI \rightleftharpoons RCOOH + R'I \tag{3}$$

Discussion

The fact that the next higher alcohol $R'CH_2OH$ corresponding to the alkyl moiety of the ester is produced in the reaction suggests that RCO_2CH_2R' is formed simply via esterification of $R'CH_2OH$ by the acid coming from the acyl moiety of the starting ester. Thus our initial hypothesis is confirmed: the mechanism of the hydrocarbonylation of esters in the presence of Co-Ru catalytic systems must be close to that of alcohol homologation [17]. An important step in this mechanism involves the formation of the olefin corresponding to ROH by an apparent E_1 mechanism followed by the normal hydroformylation to RCHO and subsequent hydrogenation to the alcohol [22,23].

In this context the formation of the alkene is the key step mainly determining the yield of the next higher alcohol, though a S_N2 process cannot be completely excluded, and in fact should operate with cobalt catalysts [17]. On the basis of the usual assumptions concerning the formation of active species, the following pathways can be considered:

(i) With ruthenium in the presence of iodine, the iodoruthenium carbonyl [5] may give a species $Ru(C_nH_{2n+1})(CO)_{x-1}I_y$, which would disproportionate into an olefin and a hydridoiodoruthenium carbonyl, which in turn may be able to catalyze the hydroformylation effectively. It is known that ruthenium and iodine react with syngas under pressure to give $HRu_3(CO)_{11}^- + Ru(CO)_3I_3^-$ [18] and $[HRu_3(CO)_{11}]^-$ has been assumed to accelerate the cobalt-catalyzed hydroformylation of cyclohexene [19].
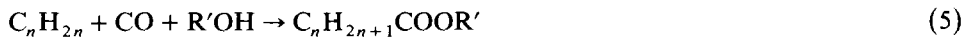
(ii) With cobalt, alkylcobalt is probably formed [20], and may subsequently undergo dehydration to the alkene or be acylated. In this respect iodine probably plays an important role by facilitating β-elimination [20]. Once the olefin has been formed, the hydroformylation should be greatly assisted by the presence of ruthenium, as shown above.

$$RuH(CO)_{x-1}Iy + C_nH_{2n+2}$$

$$\uparrow H_2$$

$$Ru(C_nH_{2n+1})(CO)_{x-1}Iy + RCO_2H$$

$$\downarrow - RuH(CO)_{x-1}Iy$$

$$RCO_2C_nH_{2n+1} \qquad \xrightarrow{CO + H_2}{}^{"Ru","I"} \qquad C_nH_{2n+2} \xleftarrow{H_2} C_nH_{2n} \xrightarrow{CO, H_2} C_nH_{2n+1}CHO \xrightarrow{H_2} C_nH_{2n+1}CH_2OH \xrightarrow{RCO_2H} RCO_2CH_2C_nH_{2n+1}$$

$$\xrightarrow{CO + H_2}{}^{"Co","I"} \qquad \nearrow -HCo(CO)_4$$

$$(C_nH_{2n+1})Co(CO)_4 + RCO_2H$$

$$\downarrow H_2$$

$$C_nH_{2n+2} + HCo(CO)_4$$

SCHEME 1

We therefore propose the tentative Scheme 1.

On the hypothesis of the olefinic intermediate, the formation of the higher acid RCH_2CO_2H and the corresponding esters can be simply accounted for in terms of a hydroxycarbonylation reaction [21].

$$C_nH_{2n} + CO + H_2O \rightarrow C_nH_{2n+1}COOH \tag{4}$$

$$C_nH_{2n} + CO + R'OH \rightarrow C_nH_{2n+1}COOR' \tag{5}$$

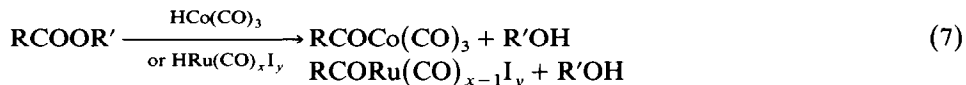$$C_nH_{2n} + CO + ROH \rightarrow C_nH_{2n+1}COOR \tag{6}$$

We should emphasize that under our conditions, direct homologation of the acid produced by disproportionation of the starting ester is not possible. Direct carbonylation of the alcohol, however, is not excluded, and has been suggested for the Ru-catalyzed hydrocarbonylation of esters [12,16].

The participation of the olefinic intermediate is at present only speculative, and was not considered for the hydrocarbonylation of esters in the presence of ruthenium-iodine catalysts [12,16].

The proposed mechanistic scheme seems to hold for the hydrocarbonylation of ethyl esters, propyl acetates and t-butyl acetate [14]. The iodide promotor, certainly plays an important and complex role, as can be seen from the Tables. Elemental iodine is a good disproportionation catalyst, since much acid is formed, while I^- is not, though it should be a good promotor for the formation of the iodoruthenium carbonyl anion [8]. The possibility of forming $RCHICH_2CoL_n$ (L_n = ligands) can account for the formation of the olefin via β-elimination.

With primary alcohols the S_N2 pathway must be taken into account, as implied by Pretzer's arguments [17], and is quite plausible, since it involves the strong nucleophile I^- (the ethyl esters give more of the propyl esters when LiI is present). The olefinic intermediate, however, is likely to be formed; n-propyl and isopropyl acetates both give n- and isobutyl acetates. With secondary alcohols there should also be competition between the assumed E_1 and S_N2 mechanisms; in this case, elemental iodine is a better promotor than LiI (cf. the reactions with isopropylacetate). The tertiary alcohol examined does not need any promotor, since the E_1 mechanism operates fully, leading to isoamyl alcohol and neopentanol in better yield than when I_2 or LiI are employed.

It should finally be observed that with the ionic iodide promotor more of the alcohols are produced (R′OH and R′CH$_2$OH) than in the corresponding reaction in the presence of iodine. The alcohols could be formed either by hydrolysis or according to eq. 7.

$$RCOOR' \xrightarrow[\text{or } HRu(CO)_xI_y]{\text{HCo(CO)}_3} \begin{array}{l} RCOCo(CO)_3 + R'OH \\ RCORu(CO)_{x-1}I_y + R'OH \end{array} \tag{7}$$

This reaction could be catalyzed by I$^-$. This would mean that the higher ester RCO$_2$CH$_2$R′ can also undergo this reaction, regenerating the higher alcohol R′CH$_2$OH unless the concentration of the acid RCO$_2$H is increased (e.g., by adding some iodine), thus shifting the equilibrium toward the ester, and this is, indeed, the case (see Table 5). Mechanistic investigations of the homologation of C$_2$, C$_3$, C$_4$ alcohols are in progress.

Conclusion

This study shows that the catalytic Co-Ru-I$_2$ system permits the homologation of the alkoxy moiety of carboxylic esters, especially for ethyl esters. Higher alkyl groups are more difficult to homologate: butyl acetates give poor yields of amyl acetates, except t-butyl acetate which is easily homologated into isoamyl and neopentyl acetate without any promotor. The effect of the added ruthenium cocatalyst is believed to aid to the formation of the olefin derived from the alkyl moiety and to increase the catalytic activity of the cobalt compound in the subsequent hydroformylation reaction. Also the rapid reduction (due to the presence of ruthenium and to the high temperature) of the aldehydes formed into the less reactive alcohols limits the number of by-products. The higher alcohol produced is esterified by the acid issued from the acyl moiety of the starting ester formed by disproportionation, hydrolysis or any other way. To this respect, combination of an ionic iodide with iodine is an improved promoting system for the homologation of the alkoxy moiety.

Finally, it should be emphasized that with the catalytic system used in this study, homologation of the alkoxy moiety is the dominant process at variance with Braca's [12] and Lütgendorf's results [16].

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