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ACTIVITY OF RUTHENIUM/IODINE CATALYSTS FOR THE CARBONYLATION OF ESTERS TO GIVE CARBOXYLIC ACIDS *

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Summary

Homogeneous ruthenium/iodide systems under a pressure of carbon monoxide effectively catalyze the isomerization of methyl formate to acetic acid with yields in the range of 70%. If alkyl acetates are treated with CO/H_2, the dominant process is the carbonylation of the alkoxy moiety rather than the homologation of the acetyl or alkoxy moieties; e.g. n-butyl acetate is converted mainly into valeric acid and its derivatives, along with acetic acid and butane. Only in the case of methyl acetate is homologation of the alkoxy moiety, to give ethyl acetate along with acetic acid, the major process. This duality of behaviour can be rationalized in terms of η^2-acetyl intermediates, which can be hydrogenated to ethanol rather than hydrolyzed to acetic acid. Ester carbonylation is shown to be fast compared with alcohol carbonylation or acid homologation; esters are probably intermediates in the last process.

Introduction

There is much interest in the use of ruthenium compounds in homogeneously catalyzed syntheses of oxygenated compounds from CO/H_2 by direct or indirect processes. Thus, the ruthenium catalyzed hydrogenation of CO at pressures of > 1000 bar yields methanol and methyl formate, as was reported by Keim et al. [1] and by Bradley [2]. Addition of iodine or iodides was found by Dombek to enhance the formation of higher oxygenated products such as ethylene glycol and ethanol, and the pressure can be reduced well below 1000 bar [3]. Low melting quaternary phosphonium salts were used as the solvent by Knifton et al., and this led to formation of alcohols under remarkably mild conditions [4]. Indirect syntheses

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catalyzed by ruthenium/iodine systems were investigated by Braca et al.; e.g. the formation of ethyl acetate by homologation of methyl acetate or carbonylation/homologation of dimethyl ether [5]. Using similar catalysts, Knifton et al. observed homologation of carboxylic acids; e.g., at 270 bar CO/H_2/220°C acetic acid is converted into propionic acid with a 37% selectivity, higher acids also being formed [6]. Following our studies of hydrocarbonylation reactions [7], we became interested in the problem of why ruthenium/iodine systems under similar conditions cause homologation of methanol derivatives to give ethanol derivatives but convert acetic and higher acids into the homologous acids, although essentially the same ruthenium acyl intermediates are involved in both cases. We therefore decided to study the carbonylation/hydrocarbonylation of various alkyl acetates as well as of methyl formate. Homogeneous ruthenium systems are well-known hydrogenation catalysts for substrates such as aldehydes and esters [8,9], and our results indicate they are also effective catalyst for ester carbonylation, and further insight into the mechanism of processes such as carboxylic acid homologation has been obtained. Our results are consistent with those of recent study by Braca et al. in which the carbonylation and homologation of formic and higher esters were investigated and found to yield homologous esters, alcohols and hydrocarbons [10].

Experimental

The carbon monoxide ($< 1\%$ H_2) and synthesis gas ($CO/H_2 = 1/1$) were of technical purity and were donated by BASF. The hydrogen came from Messer Griesheim. Methyl iodide, methyl formate, ethanol, acetic acid and the acetates were commercial products, and were used without further purification. $RuCl_3 \cdot 3H_2O$ was donated by Degussa AG (Hanau).

Catalytic runs were carried out in magnetically stirred 150 ml autoclaves made from Hastelloy C4, using glass liners and glass coated stirring bars. In a typical experiment ruthenium chloride, methyl iodide and the substrate (ester) were introduced into the autoclave, which was flushed with the appropriate gas (CO or CO/H_2) and pressurized to 70% of the final pressure. By use of an electrical heating jacket the reaction temperature was reached within 30 min, after which the pressure was adjusted to the required value. This pressure was maintained throughout the reaction by means of a pressure control system. After the reaction the autovlave was cooled to room temperature with pressurized air and vented into a gasometer ("Linde Plastigas" bag). Gaseous products were analyzed by GLC on a Fischer Gas Partioner, Model 1200 using 5.5 m × 1/8″ 37% OV 101 and 3.15 m × 3/16″ molecular sieve (13A) columns. Quantitative determination of liquid products was achieved by using diglyme as the internal standard. The analysis was carried out with a 20 m WG 11 glass capilary column, ID 0.25 mm (WGA Düsseldorf) at 30–230°C (25°C/min) using a Carlo Erba 2300 AC instrument equipped with a flame ionization detector. Response factors and details of the data processing are given in ref. 11.

For ester carbonylation at varying syngas compositions, the autoclaves were initially pressurized with $CO/H_2 = 1/1$, and the gas consumed by the reaction was replaced by CO for $P_{CO}/P_{H_2} + P_{CO} > 0.5$ and by H_2 for $P_{CO}/P_{CO} + P_{H_2} < 0.5$ (cf. Table 3).

Results and discussion

Formation of acetic acid by isomerization of methyl formate is almost quantitative when rhodium [12] or iridium [13,14] catalysts are used in the presence of methyl iodide or other iodine compounds.

$$HCO_2CH_3 \rightarrow CH_3CO_2H \qquad (1)$$

Hydrocarbonylation of methyl formate at low concentrations of ruthenium/phosphine/methyl iodide catalysts was studied by Keister et al., and shown to give some ethanol and ethyl formate, as well as traces of 1,1-dimethoxyethane and methylacetate [15]. Detailed studies by Braca et al. revealed that the catalyst activity was greater in the absence of phosphines, and that use of acetic acid as the solvent was beneficial [5,10]. A rather complex mixture was observed, the predominant processes being formyl hydrogenation, methyl carbonylation, and homologation, leading to alcohols, ethers, esters, and hydrocarbons.

In our experiments, use of ruthenium chloride/methyl iodide (molar ratio 1/5) in neat methyl formate at 28.0 MPa of CO/H_2 (1/1) at 220°C led to formation of methyl acetate and acetic acid with a combined selectivity of $< 50\%$, along with hydrocarbons and ethers. However, under a pressure of technical grade carbon monoxide (25.0 MPa) carbonylation was remarkably selective as shown in Table 1. The amount of methyl formate converted and the acetic acid yield both increased with the catalyst concentration and the reaction time. Whereas at low conversions methyl acetate, formed by transesterification (eq. 2), dominates, at high conversions acetic acid is the major product, obtained in yields of 60–70%.

$$CH_3CO_2H + HCO_2CH_3 \rightleftharpoons CH_3CO_2CH_3 + HCO_2H \qquad (2)$$

Gaseous products such as CO_2 and CH_4 are also found; for example, in amounts of 317 and 130 mmol respectively, in run 3. Reactions contributing to the formation of these compounds are methyl formate decomposition (eq. 3) and the water gas shift (WGS) reaction (eq. 4).

$$HCO_2CH_3 \rightarrow CH_4 + CO_2 \qquad (3)$$

$$HCO_2H \rightleftharpoons CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (4)$$

Reaction 3 is thermodynamically very favourable [13], and catalysis of WGS reaction by soluble ruthenium systems is a well established process [16].

TABLE 1

ISOMERIZATION OF METHYL FORMATE WITH $RuCl_3/MeI$ AS CATALYST (Molar ratio $CH_3I/RuCl_3 \cdot 3H_2O = 5$, 1000 mmol methyl formate, 220°C, 25.0 MPa CO, 8 h)

Run	$RuCl_3$ (mmol)	Conversion (mol%)	Products (mmol)	
			CH_3CO_2H	$CH_3CO_2CH_3$
1	0.75	22.2	15.5	75.1
2	3.0	84.4	189.5	269.4
3	6.0	99.7	487.3	157.1
4	6.0 [a]	99.7	657.3	50.8

[a] Reaction time 16 h.

The catalytic activity for methyl formate isomerization is typically in the range of 19.1 mol (AcOH + AcOMe)/mol Ru · h (run 2). Although such activity is poorer than that of rhodium and of iridium systems [12–14], ruthenium catalysts are of potential commercial interest because of their lower cost. In addition, product separation is easier since the only significant side products (CH_4, CO_2) are gases and methyl acetate can be recycled to give additional acetic acid.

Having established the high carbonylation activity of ruthenium systems in the case of methyl formate isomerization we were interested to study their behaviour in synthesis of carboxylic acids from higher esters and synthesis gas. As substrates alkyl acetates with C_1–C_6 alkyl groups were used. The following primary reactions were all possible:

$$CH_3CO_2R + 2H_2 \rightarrow CH_3CH_2OH + ROH \quad (5)$$

$$CH_3CO_2R + CO + 2H_2 \rightarrow CH_3CH_2CO_2H + ROH \quad (6)$$

$$CH_3CO_2R + CO + H_2O \rightarrow RCO_2H + CH_3CO_2H \quad (7)$$

$$CH_3CO_2R + 2CO + 2H_2 \rightarrow RCH_2CO_2H + CH_3CO_2H \quad (8)$$

$$CH_3CO_2R + H_2 \rightarrow RH + CH_3CO_2H \quad (9)$$

The acetyl group can be hydrogenated to give ethanol (eq. 5) or homologated to give propionic acid (eq. 6). The alkoxy moiety can be carbonylated to give the homologous carboxylic acid (eq. 7) which in turn can be homologated (eq. 8). Furthermore the alkoxy moiety can be hydrogenated to the corresponding alkane (eq. 9). As by-products, alcohols (eqs. 5, 6) or acetic acid (eqs. 7, 9) can be formed by hydrolysis. The products of eqs. 5–9 may undergo a variety of secondary reactions such as esterification, transesterification, hydrogenation, carbonylation, and homologation, resulting in a complex product mixture.

Table 2 summarizes the results obtained from the reaction of C_1–C_6 acetates and gives the selectivities for alkoxy carbonylation (A), alkoxy homologation (B), and acetyl homologation (C). Except for methyl acetate the dominant process is carbonylation of the alkoxy moiety according to eq. 7. The effects of changing the reaction conditions such as temperature, pressure, catalyst concentration, and ruthenium iodine ratio had been determined in a preliminary study in order to optimize the yields of carboxylic acid [11].

In the case of methyl acetate (run 5) it is impossible to decide whether the dominant product, acetic acid, comes from ester hydrolysis or methyl carbonylation. However, in contrast to the behaviour of the other substrates homologation of the methoxy moiety to ethyl acetate becomes an important process, along with acetyl homologation. This result is consistent with those reported by Braca et al. [5].

Hydrocarbonylation of ethyl acetate (run 6) gives, in addition to acetic acid, mainly propionic acid and ethyl propionate with a combined selectivity of about 46%. The high yield of acetic acid indicates that the propionic acid originates from the ethoxy part of the ethyl acetate (eq. 7) rather than from the acetyl part (eq. 6). In the case of the higher alkyl acetates, such as isopropyl acetate, it is evident that the isobutyric acid and butyric acid produced, must come from the carbonylation of the isopropoxy moiety. Unfortunately the yield of C_4 acids is rather limited due to ester hydrogenolysis to give acetic acid and propane (eq. 9), the latter being detected in the gaseous phase in 80% yield. Ester hydrogenolysis seems to be facilitated by branching of the alkoxy moiety.

TABLE 2

RUTHENIUM CATALYZED REACTIONS OF ALKYL ACETATES WITH CO/H_2 (A = alkoxy carbonylation; B = alkoxy homologation; C = acetyl homologation; 2.0 mmol $RuCl_3 \cdot 3H_2O$, 20 mmol CH_3I, 220°C, 25.0 MPa CO/H_2 (1/1), 6 h)

Ester (mmol) (Run)	Conversion (%)	Products (mmol)		Type of reaction	Selectivity (mol%)
$CH_3CO_2CH_3$ [a]	58.8	CH_3CO_2H	425.9	A	90.5
800		$CH_3CO_2C_2H_5$	70.8	B	15.1
(5)		$C_2H_5CO_2H$	9.3	C	2.0
		$C_2H_5CO_2C_2H_5$	0.8	B,C	0.2
$CH_3CO_2C_2H_5$ [b]	74.6	CH_3CO_2H	308.5		
625		$C_2H_5CO_2H$	160.9	A	34.5
(6)		$C_2H_5CO_2C_2H_5$	57.0	A	12.2
		$C_3H_7CO_2H$	6.2	A	1.3
		$C_3H_7CO_2C_2H_5$	2.2	A	0.5
		$(CH_3)_2CHCO_2H$	1.3	A	0.3
$CH_3CO_2CH(CH_3)_2$	96.5	CH_3CO_2H	393.0		
500		$C_3H_7CO_2H$	23.0	A	4.8
(7)		$(CH_3)_2CHCO_2H$	58.0	A	12.0
		$(CH_3)_2CHCH_2CO_2H$	1.0	A	0.3
$CH_3CO_2C_4H_9$	90.5	CH_3CO_2H	294.5		
500		$CH_3CO_2C_2H_5$	14.5		
(8)		$C_2H_5CO_2H$	19.5	C	4.3
		$C_2H_5CO_2C_2H_5$	1.0	C	0.2
		$C_4H_9CO_2H$	155.2	A	34.3
		$C_4H_9CO_2C_4H_9$	27.4	A	6.1
		$C_5H_{11}CO_2H$	11.8	A	2.6
		C_4H_{10}	100.0		
$CH_3CO_2C_5H_{11}$ [c]	77.0	CH_3CO_2H	299.6		
500		$C_5H_{11}CO_2H$	84.8	A	22.0
(9)		$C_6H_{13}CO_2H$	1.6	A	0.4
		C_5H_{12}	115.4		
$CH_3CO_2C_6H_{13}$	70.0	CH_3CO_2H	228.0		
500		$C_2H_5CO_2H$	3.0	C	0.9
(10)		$C_3H_7CO_2H$	1.0	C	0.3
		$C_6H_{13}CO_2H$	47.0	A	13.4
		$C_7H_{15}CO_2H$	0.6	A	0.2
		C_6H_{14}	35.0		

[a] 3.2 mmol $RuCl_3 \cdot 3\ H_2O$, 32 mmol CH_3I; acetic acid at least partially derived from acetate hydrolysis. [b] 2.5 mmol $RuCl_3 \cdot 3H_2O$, 25 mmol CH_3I; acetyl homologation and alkoxy carbonylation cannot be differentiated. [c] C_5H_{11} = isoamyl.

The yield of n-butane in the hydrocarbonylation of n-butyl acetate (run 8) is only 22% and the major reaction is alkoxy carbonylation to give valeric acid and butyl valerate with a combined selectivity of 40% (run 8). Homologation of the acetyl moiety is evidently less favoured, and propionic acid as well as ethyl propionate are formed only with a combined selectivity of 4.5%. Somewhat similar behaviour was reported recently by Braca et al. [10], although formation of esters rather than of acids was observed, along with a considerable amount of alkoxy homologation to pentyl derivatives. This different product distribution can be attributed to the milder reaction conditions used by Braca et al., such as lower temperature, pressure, and catalyst concentration.

In the case of higher alkyl acetates the catalytic activity and the alkoxy carbonylation selectivity are reduced. Thus, isoamyl acetate conversion is only 77%, with isohexanoic acid and isoheptanoic acid selectivities of 22% and 0.4%, respectively (run 9). Hexyl acetate is transformed at a 70% conversion, with a 13% selectivity, to heptanoic acid (run 10). Possibly the reduced catalytic activity in the case of the higher alkyl acetates is due to the more hydrophobic nature of the esters and of the corresponding ruthenium intermediates.

The use of other acetates as substrates yielded at best trace amounts of the expected carboxylic acid. Thus, tertiary butyl acetate gave pivalic acid in 3% yield along with a complex product mixture which included C_1–C_4 hydrocarbons and acetic acid. Benzyl acetate gave no carbonylation products, although carbonylation of benzyl alcohol with rhodium catalysts is a known process [17]. Instead, the hydrogenation products toluene and benzylated toluenes were found. As expected, phenyl acetate gave only traces of benzoic acid, and the main process was formation of 2-acetyl phenol in a Fries type rearrangement, and the isomeric ethyl phenols were present as hydrogenation products. Since no benzene could be detected, formation of phenyl ruthenium intermediates appears to be markedly disfavoured under these conditions.

The carbonylation of alkyl acetates is highly dependent on the syngas composition, as is shown in Table 3 for butyl acetate. Whereas in the case of methyl formate isomerization the best yields of acetic acid were observed with pure CO, in the case of butyl acetate the degree of conversion increased with the partial pressure of hydrogen and the highest yields of valeric acid and its derivatives were obtained at a 1/1 CO/H_2 molar ratio. Homologation of the acetyl moiety is clearly less favoured than alkoxy carbonylation under all the conditions examined, but the yield of propionic acid increases with P_{H_2}, as does the yield of acetic acid formed mainly through reactions (7–9). Similar behaviour was observed by Braca et al. in ester homologation [10] and by Knifton in acid homologation [6]. The observation that

TABLE 3

EFFECT OF SYNGAS COMPOSITION ON BUTYL ACETATE CARBONYLATION (500 mmol $CH_3CO_2C_4H_9$, 2.0 mmol $RuCl_3 \cdot 3H_2O$, 20 mmol C_3I, 220°C, 25.0 MPa, 6 h)

$P_{CO}/P_{CO}+P_{H_2}$	1	> 0.5 [a]	0.5	< 0.5 [a]
Run	11	12	8	13
Conversion (%)	19.9	61.2	90.5	91.4
Products (mmol)				
CH_3CO_2H	47.0	226.0	294.5	458.0
$CH_3CO_2C_2H_5$		8.0	14.5	16.0
$C_2H_5CO_2H$		14.0	19.5	23.0
$C_2H_5CO_2C_2H_5$			1.0	
$C_4H_9CO_2H$	9.0	64.0	155.2	150.0
$C_4H_9CO_2C_4H_9$	27.6	50.0	27.4	21.0
$C_5H_{11}CO_2H$		1.0	11.8	9.0

[a] see Experimental part.

hydrogen enhances the activity of ruthenium catalysts in ester carbonylation indicates that ruthenium hydrides are involved in the catalytic cycle.

To evaluate the activity of ruthenium/iodine catalysts for synthesis of carboxylic acid from esters, comparative experiments were carried out with ethyl acetate (run 6), acetic acid (run 14), and ethanol (run 15). As shown in Table 4, propionic acid is the principal product in all cases. However, the catalytic activity for ethyl acetate carbonylation exceeds that of ethanol carbonylation by a factor of three and that for acid homologation by a factor of five. It is also noteworthy that in the case of acetic acid homologation considerable amounts of ethyl acetate are formed. This indicates that carboxylic acid homologation is a two step process, involving, in the case of acetic acid slow hydrogenation to ethyl acetate, followed by rapid carbonylation of the latter to propionic acid, and so different catalytic species may be involved in the hydrogenation and carbonylation steps. This picture differs from that advanced by Knifton [6], who proposed immediate hydrogenation/carbonylation via RCORu, RCH_2Ru, and RCH_2CORu species without any alcohol or ester intermediates.

The high reactivity of ethyl acetate compared to ethanol in carbonylation may also be due to its easier conversion into ethyl iodide, acetic acid being a better leaving group than water (see eqs. 10 and 11).

$$ROH + HI \rightarrow RI + H_2O \tag{10}$$

$$RCO_2R' + HI \rightarrow R'I + RCO_2H \tag{11}$$

The alkyl iodides bring about alkylate ruthenium complexes via oxidative addition or nucleophilic substitution pathways (Scheme 1). An alternative route, in which alcohols or esters directly alkylate a hydridic ruthenium intermediate, has been proposed by Braca et al. [10] and would lead to a similar pattern of reactivity.

Remarkably, addition of water hardly affects the carbonylation of ethyl acetate, although eq. 7 requires stoichiometric amounts of water. As shown in Table 4 (run 16), both the activity and yield of propionic acid are virtually the same as with neat

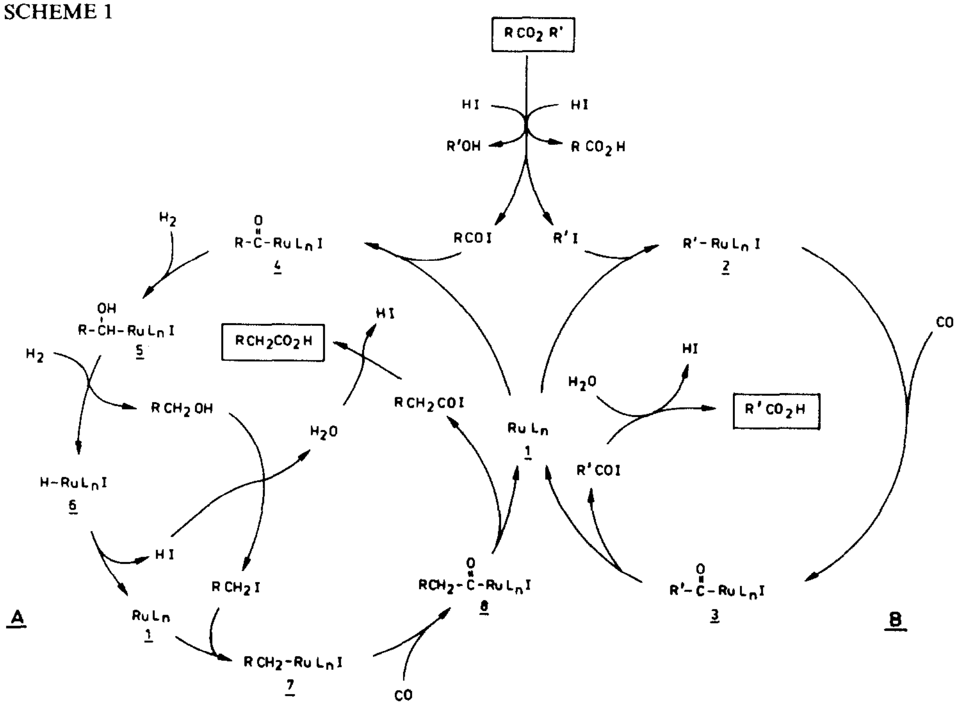
TABLE 4

CARBONYLATION OF ETHYL ACETATE, ACETIC ACID, AND ETHANOL (2 mmol $RuCl_3 \cdot 3H_2O$, 20 mmol CH_3I, 220°C, 25.0 MPa CO/H_2 (1/1), 6 h)

Substrate (mmol)	$CH_3CO_2C_2H_5$ [a] 625	CH_3CO_2H 1000	C_2H_5OH [b] 1087	$CH_3CO_2C_2H_5$, 500 H_2O, 500
Run	6	14	15	16
Products (mmol)				
CH_3CO_2H	308.5	~ 900		298.7
$CH_3CO_2C_2H_5$	159.0	22.0	5.7	108.1
C_2H_5OH			~ 1000	
$C_2H_5CO_2H$	160.9	36.0	57.8	128.9
$C_2H_5CO_2C_2H_5$	57.0	1.0		49.6
$C_3H_7CO_2H$	6.2		1.5	3.1
$C_3H_7CO_2C_2H_5$	2.2		1.7	
$(CH_3)_2CHCO_2H$	1.3			
Activity, mol C_{3+}-product/mol Ru·h	15.2	3.1	5.1	15.1

[a] 2.5 mmol $RuCl_3 \cdot 3H_2O$, 25 mmol CH_3I. [b] 280 bar CO/H_2 (1/1).

SCHEME 1



ethyl acetate (run 6). In the latter case the water required according to the stoichiometry of eq. 7 is provided by side reactions such as homologation and hydrogenation reactions. In keeping with this picture, the liquid product from acid homologation (run 14) contained about 30% water (by weight; compared to 2–3% in the case of ester carbonylation as determined by the Karl Fischer method [18]).

As shown in Table 2, the alkoxy moiety of alkyl acetates reacts more readily than the acetyl moiety by a factor of about eight. This appears to be due to the relative rates of ruthenium alkyl carbonylation and acyl hydrogenation, respectively. On the other hand, the formation of the ruthenium acetyl intermediate must be disfavoured, since reaction of HI with alkyl acetates leads to alkyl iodides (eq. 11) rather than to acetyl iodide (eq. 12).

$$RCO_2R' + HI \rightarrow RCOI + R'OH \qquad (12)$$

The acetic acid formed as a by-product of alkyl acetate carbonylation according to eq. 7 must also have an accelerating effect on the overall process, since in ruthenium catalyzed methyl acetate homologation [19] and in rhodium catalyzed methanol carbonylation [20] enhanced reactivities have been observed upon addition of acetic acid.

Our results are in accordance with the mechanistic scheme depicted in Scheme 1. The main reaction is carbonylation of the alkoxy moiety (cycle **B**), in which an alkyl iodide R'I adds oxidatively to the ruthenium species **1**, and this is followed by CO insertion and reductive elimination of an acyl iodide, which then is hydrolyzed to give the acid $R'CO_2H$. In the less favoured homologation of the acyl moiety (cycle

A) an acyl iodide adds oxidatively to **1**; the resulting acyl complex **4** is hydrogenated stepwise to the hydridic species **6** and to the alcohol RCH_2OH, which is transformed to RCH_2I. This alkyl iodide is then carbonylated via intermediates analogous to those in the mechanism suggested by Knifton for carboxylic acid homologation [6]. The unsaturated ruthenium species **1** is probably of the type $[RuI_x(CO)_y]^{n-}$, since the anionic system $[RuI_3(CO)_3]^-$ has been shown to be readily produced from various ruthenium precursors and iodine compounds under catalytic conditions [3,6,21].

Important side reactions include hydrocarbon formation from alkyl ruthenium complexes **2** ($\rightarrow$ R'H) and **7** ($\rightarrow RCH_3$). Also, the acyl complex **3** of cycle **B** can be hydrogenated according to cycle **A** to give the homologated acid $R'CH_2CO_2H$. The acids produced will undergo esterification and transesterification, and ethers will be also formed, by reaction of alkyl iodides with alcohols.

In methyl formate isomerization ($R = H$, $R' = CH_3$) only cycle **B** operates, and the formic acid produced in reaction 11 decomposes to CO and H_2O, which are consumed in acetic acid formation. In contrast to higher alkyl acetates, methyl acetate undergoes alkoxyl homologation to ethyl acetate [5]. Obviously the acetyl ruthenium species **3** is more prone to hydrogenation than to reductive elimination/hydrolysis. This can be understood by assuming an η^2-acetyl intermediate which is preferentially hydrogenated, while with higher esters η^1-acyl species can be expected. Model complexes such as $Ru(\eta^2\text{-}COCH_3)I(PPh_3)CO$ have been isolated by Roper et al. [22].

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