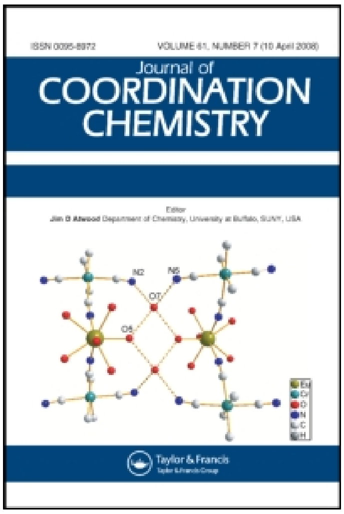

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New media in homogeneous catalysis: wet sodium or tetrabutylammonium hydrogensulfate salts for reppe syntheses catalyzed by a ru(ii) carbonyl complex

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NEW MEDIA IN HOMOGENEOUS CATALYSIS: WET SODIUM OR TETRABUTYLAMMONIUM HYDROGENSULFATE SALTS FOR REPPE SYNTHESES CATALYZED BY A Ru(II) CARBONYL COMPLEX

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The ruthenium(II) complex *fac*-[$Ru(CO)_2(H_2O)_3(C(O)C_2H_5)$][$CF_3SO_3$] dissolved in aqueous tetrabutylammonium hydrogensulfate ([$(CH_3(CH_2)_3)_4N$][HSO_4]) or sodium hydrogensulfate ($NaHSO_4$) catalyzes the hydrocarboxylation of ethylene to propionic acid and additionally produces minor amounts of hydrocarbonylation products (diethyl ketone and propanal), under water-gas shift reaction conditions. This system is stable with a selectivity of 90% to propionic acid for high ethylene conversion. A turnover frequency of propionic acid, $TOF(C_2H_5CO_2H)/24\,h = 5 \times 10^3$ ($TOF(C_2H_5CO_2H) = ([(\text{moles of } C_2H_5CO_2H)/(\text{moles of Ru}) \times rt)] \times 24\,h$) was achieved for $Ru = 7.45 \times 10^{-4}$ mol, $[(CH_3(CH_2)_3)_4N][HSO_4] = 80\,g$ (2.36×10^{-2} mol); $H_2O = 40\,g$ (2.22 mol); $CO = C_2H_4 = 20\,g$ (total pressure = 88 atm); $T = 150°C$ by a reaction time (rt) of 2.87 h. The countercation (sodium or tetrabutylammonium), the ruthenium concentration and the hydrogensulfate/H_2O ratio of the medium affect the catalytic reaction. A nonlinear dependence on total ruthenium concentration was shown. The data are discussed in terms of a potential catalytic cycle. Formation of propionic acid comes from hydrolysis, and formation of diethyl ketone and propanal comes from hydrogenolysis of the Ru-ketyl and Ru-acyl complexes, respectively.

Keywords: Reppe synthesis; Ruthenium complex; Ethylene; Carbon monoxide; Propionic acid; Diethyl ketone

INTRODUCTION

Reppe syntheses involve addition of hydrogen and a carboxyalkyl group to an olefinic substrate, a hydrocarboxylation process. Since the early work of Reppe [1] the relationship between the water-gas shift reaction [WGSR, Eq. (1)] and olefin

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hydrocarboxylation with CO/H_2O [Eq. (2)] in alkaline solution has been recognized. Pettit *et al.* [2] reported the generalization of this reaction with other metal carbonyl complexes. Mechanistic aspects of the Reppe reaction have been discussed [3] on the basis of attack by strong nucleophile $(OH)^-$ on a coordinated CO ligand of a metal carbonyl to generate a hydride carbonyl intermediate both for H_2 formation in the WGSR and for the production of organic products in the presence of an olefin.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$

$$CH_2{=}CHR + CO + H_2O \rightarrow CH_3CHR(CO_2H) \qquad (2)$$

The nature of the medium can dramatically affect a homogeneous catalytic reaction. Polar, non-traditional solvents (ionic liquids) have been investigated [4–6] and allowed facile catalyst recovery from biphasic systems [7]. In this field, we observed that the industrially relevant Reppe syntheses [8,9] could be performed in an unprecedented medium constituted by wet inorganic hydrogensulfate salts in the liquid phase.

Recently, some examples of Reppe syntheses promoted by homogeneous rhodium/I^- [10], $Co_2(CO)_8$-diphos/THF-water [11] and water-soluble palladium [12] catalysts have been reported. However, little is known about the hydrocarboxylation of CO/ethylene promoted in aqueous media by ruthenium complexes bearing an acyl ligand.

In this article, we report our preliminary observations on the influence of reaction conditions (nature of cocatalyst, [cocatalyst] and [Ru]) on the catalytic hydrocarbonylation of ethylene by *fac*-$[Ru(CO)_2(H_2O)_3(C(O)C_2H_5)](CF_3SO_3)$ dissolved in a salty inorganic medium.

EXPERIMENTAL

Materials and Instrumentation

Tetrabutylammonium hydrogensulfate ($(CH_3(CH_2)_3)_4N(HSO_4)$, 97%) from Aldrich and sodium bisulfate ($NaHSO_4{\cdot}H_2O$) from Carlo Erba were used as received. CaO containing ethyl violet indicator from Carlo Erba was used as received. The aqueous solution of the ruthenium(II) complex *fac*-$[Ru(CO)_2(H_2O)_3(C(O)C_2H_5)](CF_3SO_3)$ was prepared by the literature method [13]. The solution was dried until the formation of a pale-yellow solid. Water was distilled and stored in an atmosphere of argon (Rivoira). CO (Rivoira) and ethylene (Praxair) were used as received.

Organic products were analyzed with a Dani Model 8400 gas chromatograph equipped with a flame ionization detector and a $2\,m \times 1/8\,in$ Carbowax W (80–100 mesh) packed column, using He (Rivoira) as carrier gas. The potentiometric titration and determinations of pH were performed on a Crison model 2001 pH-meter.

Catalyst Testing

Catalytic runs were carried out in a 400-cm^3 mechanically stirred, stainless-steel autoclave charged with 40-cm^3 of water, a given amount (typically 7.45×10^{-4} mol) of $[Ru(CO)_2(H_2O)_3(C(O)C_2H_5)](CF_3SO_3)$, variable amounts of tetrabutylammonium hydrogensulfate or sodium bisulfate and pressurized with CO and ethylene (total pressure = 88 atm at 25°C). The autoclave was immersed in an oil bath at 150 ± 1°C for a given time. The pressure and temperature were chosen to average the previously reported systems [14–17]. At the end of the reaction the amounts of CO_2 and propionic acid formed were determined by the weight gained by bubbling the gases through a glass column packed with CaO and by potentiometric titration of an aliquot of the reaction solution with NaOH (0.1 M), respectively.

RESULTS AND DISCUSSION

General Aspects

Complexes of the type *fac*-$[Ru(CO)_2(H_2O)_3(C(O)C_2H_5)]^+$ (0.01 M) dissolved in 0.1 M trifluoromethanesulfonic acid (CF_3SO_3H) catalyze the hydrocarboxylation [Eq. (3)] of ethylene (30 atm) to propionic acid ($C_2H_5CO_2H$) under CO (4 atm) at 140°C [13]. Under these conditions, a $TOF(C_2H_5CO_2H)/24\,h$ (($TOF(C_2H_5CO_2H) =$ moles of $C_2H_5CO_2H$/moles of Ru/24 h) of about 370 was observed; a reductive hydrocarbonylation of ethylene to diethyl ketone ($C_2H_5C(O)C_2H_5$) [Eq. (4)] accompanied hydrocarboxylation when the $[C_2H_5CO_2H]$ formed under the catalytic conditions reaches a value > 3 M.

$$C_2H_4 + CO + H_2O \rightarrow C_2H_5CO_2H \qquad (3)$$

$$2C_2H_4 + 2CO + H_2O \rightarrow CO_2 + C_2H_5C(O)C_2H_5 \qquad (4)$$

In comparison with the results in CF_3SO_3H/water, the highest $TOF(C_2H_5CO_2H)/24\,h = 5085$ is achieved when the medium is $[(CH_3(CH_2)_3)_4N][HSO_4)]/H_2O$ (0.106 mol/mol), $Ru = 7.45 \times 10^{-4}$ mol and $CO = C_2H_4 = 20$ g at 150°C (run 5, Table I). Quantitative analysis of the formed CO_2 shows that concurrent hydrocarbonylation yielding CO_2, diethylketone [Eq. (4)] and propanal ($C_2H_5C(O)H$) [Eq. (5)] constitutes a minor reaction (90% selectivity for propionic acid). It is well known that hydrocarboxylation is favored over hydrocarbonylation. However, hydrocarboxylation of olefins is slower than hydroformylation [9]. The experimental product distribution of our system matches these observations.

$$C_2H_4 + 2CO + H_2O \rightarrow CO_2 + C_2H_5C(O)H \qquad (5)$$

Under these catalytic reaction conditions propionic acid was the principal observed product, 69% (run 1, Table I) selectivity (ethylene conversion of 51%) and 90% (run 6, Table II) of selectivity (ethylene conversion of 22.2%) for the $(CH_3(CH_2)_3)_4N(HSO_4)$/Ru and $NaHSO_4{\cdot}H_2O$/Ru systems, respectively. As shown in Tables I–III there is a systematic increase in the selectivity to propionic acid as a function of the reaction parameters.

For this highly active and selective Ru system, we explored the effects of (i) varying the nature of the inorganic salt ($[(CH_3(CH_2)_3)_4N][HSO_4]$ or $NaHSO_4$), (ii) the relative amount of H_2O and (iii) the ruthenium complex precursor concentration. These results are reported in Tables I–III.

TABLE I Catalytic hydrocarboxylation and hydrocarbonylation of ethylene promoted by *fac*-$[Ru(CO)_2(H_2O)_3(C(O)C_2H_5)][CF_3SO_3]$ in wet $[(CH_3(CH_2)_3)_4N]$ $[HSO_4]$[a]

Run	R_4NHSO_4[b] (mol)	R_4NHSO_4/H_2O[b]	*Reaction time* (h)	*Wt. of* CO_2 (g)	*Wt. of* CO_2 (mol)	*TOF* (CO_2)[c]	*CO conversion to* CO_2 (%)	*[Acid]*[d] (mol)	*TOF (Acid)*[c]	*Acid yield* (%)	*Propionic acid selectivity* (%)	*Overall yield* (%)[e]
1	0.031	0.014	6.43	4.93	0.176	562	16	0.252	1262	35	69	51
2	0.059	0.027	6.25	5.47	0.195	640	17	0.270	1391	38	68	55
3	0.118	0.053	3.98	3.23	0.115	594	10	0.344	2783	48	82	58
4	0.179	0.081	3.02	2.47	0.088	599	8	0.368	3924	52	87	60
5	0.236	0.106	2.87	2.10	0.075	535	7	0.453	5085	63	90	70

[a] $Ru = 7.45 \times 10^{-4}$ mol; $H_2O = 40$ g (2.22 mol); $CO = C_2H_4 = 20$ g (total pressure = 88 atm at 25°C); $T = 150 \pm 1$°C.

[b] $R = CH_3(CH_2)_3$.

[c] TOF(product) = [(mol of product)/(mol of Ru) × (rt)] × 24 h, where (rt) = reaction time in hours.

[d] [Acid] = [propionic acid].

[e] Overall yield (%) = % of CO conversion to CO_2 + yield (%) of propionic acid.

TABLE II Catalytic hydrocarboxylation and hydrocarbonylation of ethylene promoted by *fac*-$[Ru(CO)_2(H_2O)_3(C(O)C_2H_5)][CF_3SO_3]$ in wet $NaHSO_4$[a]

Run	*$NaHSO_4$* (mol)	*$NaHSO_4/H_2O$*	*Reaction time* (h)	*Wt. of CO_2*		*TOF (CO_2)*[b]	*CO conversion to CO_2* (%)	*[Acid]*[c] (mol)	*TOF (Acid)*[b]	*Acid yield* (%)	*Propionic acid selectivity* (%)	*Overall yield* (%)[d]
				(g)	(mol)							
6	0.030	0.014	6.90	0.70	0.025	74	2.2	0.147	685	20	90	22.2
7	0.059	0.027	6.80	0.64	0.029	69	2.0	0.153	725	21	91	23.0
8	0.119	0.053	7.96	0.61	0.022	56	1.9	0.208	842	29	94	30.9
9	0.179	0.081	6.02	0.37	0.013	45	1.2	0.312	1670	44	97	45.1
10	0.239	0.107	7.52	0.13	0.005	13	0.4	0.152	650	21	98	21.4
11	–	–	5.42	1.70	0.061	229	5.3	0.020	119	3	34	8.3

[a] $Ru = 7.45 \times 10^{-4}$ mol; $H_2O = 40$ g (2.22 mol); $CO = C_2H_4 = 20$ g (total pressure = 88 atm at 25°C); $T = 150 \pm 1$°C.

[b] TOF(product) = [(mol of product)/(mol of Ru) × (rt)] × 24 h, where (rt) = reaction time in hours.

[c] [Acid] = [propionic acid].

[d] Overall yield (%) = % of CO conversion to CO_2 + yield (%) of propionic acid.

TABLE III Effect of [Ru] on the catalytic hydrocarboxylation and hydrocarbonylation of ethylene promoted by *fac*-$[Ru(CO)_2(H_2O)_3(C(O)C_2H_5)][CF_3SO_3]$ in wet $[(CH_3(CH_2)_3)_4N][HSO_4]$[a]

Run	*[Ru] in M* (mol × 10^{-4})	*Reaction time* (h)	*Wt. of CO_2*		*TOF* (CO_2)[b]	*CO conversion to CO_2* (%)	*[Acid]*[c] (mol)	*TOF* (Acid)[b]	*Acid yield* (%)	*Propionic acid selectivity* (%)	*Overall yield* (%)[d]
			(g)	(mol)							
12	–	4.77	–	–	–	–	–	–	–	–	–
13	0.0024 (1.81)	7.30	1.17	0.042	478	4	0.082	1468	12	76	16
14	0.0099 (7.45)	3.98	3.23	0.115	594	10	0.344	2783	48	82	58
15	0.0200 (15.05)	1.43	2.43	0.087	622	8	0.331	3728	46	86	54
16	0.0298 (22.43)	1.30	3.04	0.109	571	10	0.345	2850	48	83	58
17	0.0397 (29.88)	1.75	2.68	0.096	281	8	0.399	1840	55	87	63

[a] $[(CH_3(CH_2)_3)_4N][HSO_4] = 40$ g (0.118 mol); $H_2O = 40$ g (2.22 mol); $CO = C_2H_4 = 20$ g (88 atm); $T = 150 \pm 1°C$.

[b] TOF(product) = [(mol of product)/(mol of Ru) × (rt)] × 24 h, where (rt) = reaction time in hours.

[c] [Acid] = [propionic acid].

[d] Overall yield (%) = % of CO conversion to CO_2 + yield (%) of propionic acid.

Nonpolarizing $[(CH_3(CH_2)_3)_4N]^+$ *versus* Na^+ Cations in the Ethylene Hydrocarboxylation

As shown in Tables I and II, and Fig. 1, $[(CH_3(CH_2)_3)_4N][HSO_4]$ results in higher $TOF(C_2H_5CO_2H)/24\,h$, at any explored salt/H_2O ratio. In the case of $[(CH_3(CH_2)_3)_4N][HSO_4]$ a linear dependence of $TOF(C_2H_5CO_2H)/24\,h$, with salt/H_2O ratio is observed (Fig. 1) in the $[(CH_3(CH_2)_3)_4N][HSO_4]$ concentration range of 0.031 to 0.236 mol. On the other hand the plot of $[NaHSO_4H_2O]$ is not linear in the 0.031 to 0.236 mol range. The $TOF(C_2H_5CO_2H)/24\,h$ and the overall yields increased from 685 to 1670 $(24\,h)^{-1}$ (runs 6 to 9, Table II) and from 22.2 to 45.1% respectively, reaching the highest point at $[NaHSO_4{\cdot}H_2O] = 0.179\,M$ and then decreased. However, a better hydrocarboxylation selectivity (98%, run 10, Table I) was observed for the polarizing Na^+ countercation (Fig. 2). Above $[NaHSO_4{\cdot}H_2O] = 0.179\,M$ all product formation (overall yields = 21.4%) decreased probably owing to deactivation of the catalysts.

The tetrabutylammonium salt acts as a phase-transfer catalyst [18], changing the solubility properties of a reagent so that two reactants (an organic compound and a salt) which normally do not dissolve in the same solvent can be brought together. Even though our systems are not under real phase-transfer catalyst conditions, the solubility in water of the ethylene and CO could be enhanced due to the presence of many carbon atoms (16) in the tetrabutylammonium cation. Further, we found that 2.9 and 2.4 g of ethylene were dissolved when 10-g samples of ethylene (24 atm) were in contact with two independent solutions of water (40 g)/$[(CH_3(CH_2)_3)_4N][HSO_4]$ (5.72×10^{-2} mol) and water (40 g)/$[NaHSO_4H_2O]$ (5.72×10^{-2} mol), respectively. The two mixtures were stirred for 3 h at 150°C in a 300 cm^3 stainless-steel Parr reactor and later allowed to stand at 25°C. These solubility results match the fact that the $Ru/[(CH_3(CH_2)_3)_4N][HSO_4]$ catalytic system is more active than the

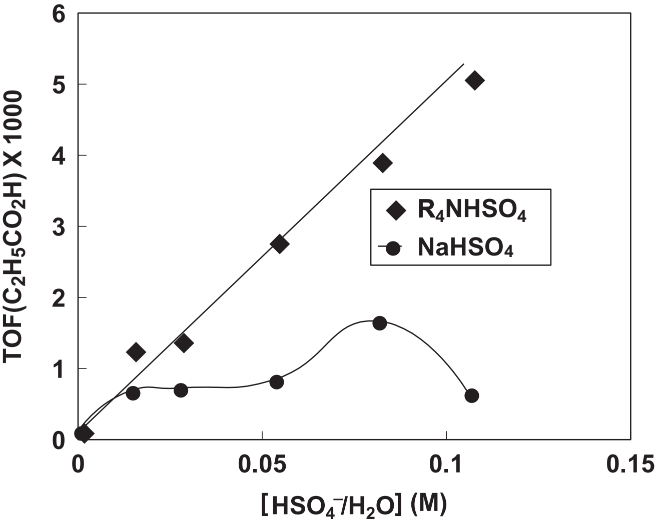


FIGURE 1 Plot of $TOF(C_2H_5CO_2H)$ *vs.* HSO_4^-/H_2O molar ratio: ◆, R_4NHSO_4, ($R = CH_3(CH_2)_3$) and ●, $NaHSO_4$. Reaction conditions: $Ru = 7.45 \times 10^{-4}$ mol; $H_2O = 40$ g (2.22 mol); $CO = C_2H_4 = 20$ g (total pressure = 88 atm at 25°C); $T = 150 \pm 1$°C. Lines drawn for illustrative purposes only.

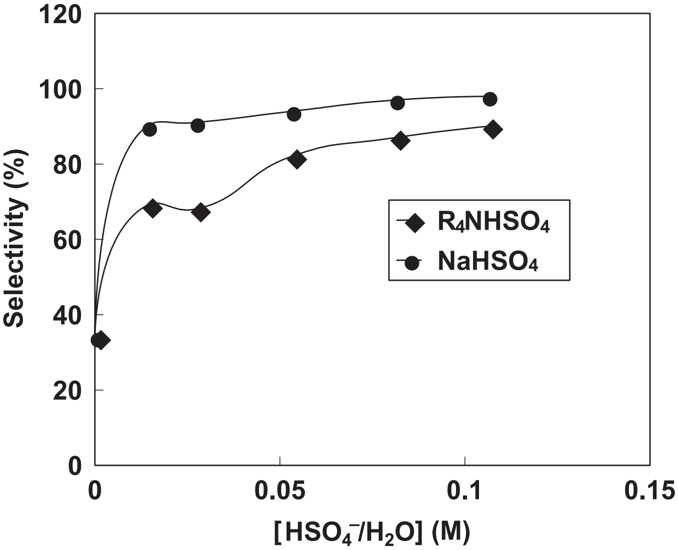


FIGURE 2 Plot of propionic acid selectivity *vs.* HSO_4^-/H_2O molar ratio: ◆, R_4NHSO_4, ($R = CH_3(CH_2)_3$) and ●, $NaHSO_4$. Reaction conditions: $Ru = 7.45 \times 10^{-4}$ mol; $H_2O = 40$ g (2.22 mol); $CO = C_2H_4 = 20$ g (Total pressure = 88 atm at 25°C); $T = 150 \pm 1$°C. Lines drawn for illustrative purpose only.

Ru/$NaHSO_4$ system. The cocatalyst salt affects both the ethylene solubility and the catalytic activity.

These two cocatalysts also play the important role of providing cations $[(CH_3(CH_2)_3)_4N]^+$ or Na^+ to the reaction medium. The interaction of these Lewis-acid cations with key ruthenium carbonyl intermediates, which can affect the catalytic activity, will be discussed in the mechanistic section.

Further, we cannot rule out the suggestion of one referee that pH may be a significant reason why more propionic acid was formed with $[(CH_3(CH_2)_3)_4N][HSO_4]$, because at the same concentrations solutions of $[(CH_3(CH_2)_3)_4N][HSO_4]$ would be more basic than solutions of $NaHSO_4$.

Further, in the absence of cocatalyst (run 11, Table II), ethylene conversion and propionic acid formation reach their lowest values, overall yield = 8.3% and $TOF(C_2H_5CO_2H)/24\,h = 119$ (3% yield), respectively. These results suggest that the salty medium formed by the dissolution in water of the cocatalyst salts could stabilize Ru catalytic species formed under the reaction conditions, enhancing their reactivity. Comparison of our aqueous $Ru/(CH_3(CH_2)_3)_4N(HSO_4)$ catalytic system ($TOF(C_2H_5CO_2H)/24\,h = 5085$ and 90% selectivity) with the aqueous $RhCl_3$/EtI catalytic system ($TOF(C_2H_5CO_2H)/24\,h = 1440$ and 85% selectivity) for the hydrocarboxylation of ethylene to propionic acid reported by Kilner and Winter [10] shows that our catalytic system is about five times more active.

Effect of Ru Concentration

Catalytic runs were carried out for a series of different ruthenium concentrations over the range (0.0024–0.0397) M (Table III). A typical run involved determination of TOF as a function of [Ru] at $[(CH_3(CH_2)_3)_4N(HSO_4] = 40$ g (0.118 mol), $[H_2O] = 40$ g under

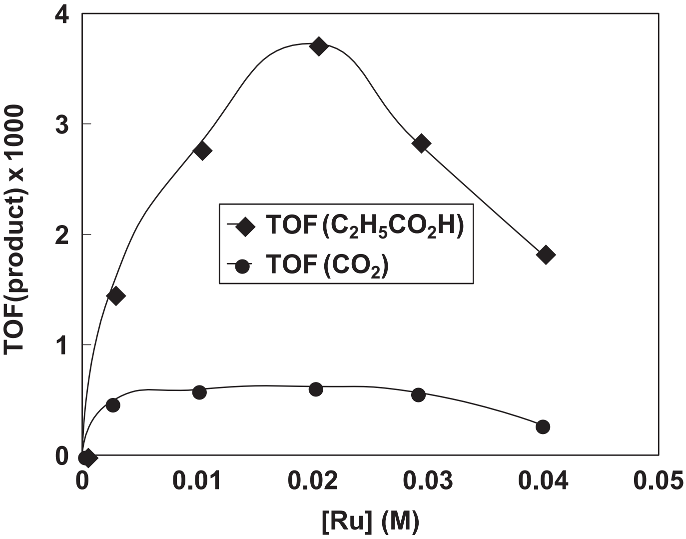


FIGURE 3 Plot of TOF(product) *vs.* [Ru]: ◆, TOF($C_2H_5CO_2H$), and ●, TOF(CO_2). Reaction conditions: $[(CH_3(CH_2)_3)_4N][HSO_4] = 40$ g (0.118 mol); $H_2O = 40$ g (2.22 mol); $CO = C_2H_4 = 20$ g (Total pressure = 88 atm at 25°C); $T = 150 \pm 1$°C. Lines drawn for illustrative purpose only.

$[CO] = [C_2H_4] = 20$ g at 150°C. Figure 3 shows the plot of TOF($C_2H_5CO_2H$)/24 h and the TOF(CO_2)/24 h values *vs.* [Ru]. An increase in [Ru] from 0.0024 M (run 13, Table III) further increased the TOF($C_2H_5CO_2H$)/24 h value, reaching a maximum at [Ru] = 0.0200 M (run 15, Table III). The activity towards propionic acid production starts decreasing at [Ru] > 0.0200 M (run 17, Table III). These findings indicate that catalyst activity does not follow a linear dependence on [Ru] in the range 0.0024–0.0397 M and suggest the intervention of less-active polynuclear species [19]. Analyses of the effects of varying the CO pressure and temperature, important parameters for the carbonylation reaction, on the activity of this Ru complex are in progress.

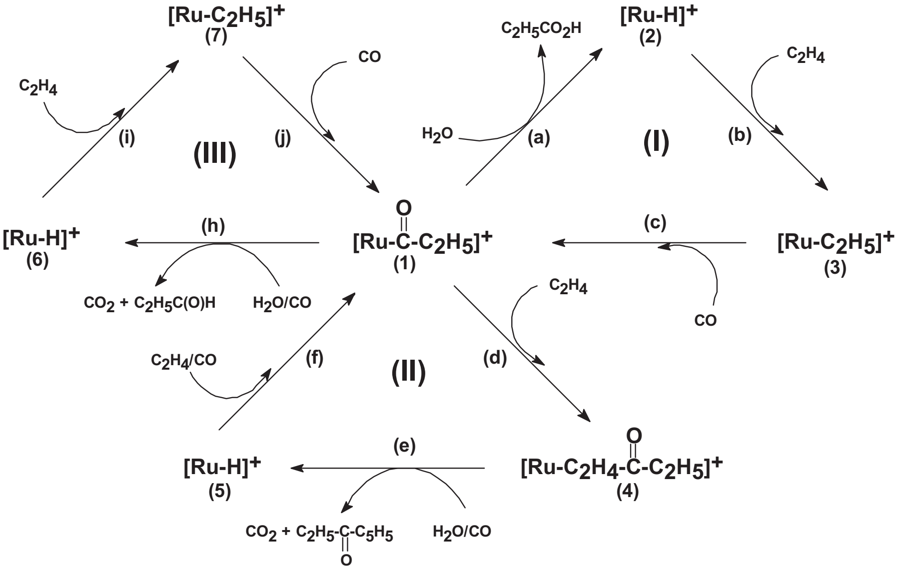
Catalysis of the Water-gas Shift Reaction

Since the early work of Reppe, the relationship between WGSR [Eq. (1)] and olefin hydrocarboxylation/hydrocarbonylation with CO/H_2O in alkaline solution has been recognized [3]. To extend this relationship to the present Ru/salty medium systems, a mixture of *fac*-$[Ru(CO)_2(H_2O)_3(C(O)C_2H_5)][CF_3SO_3]$ (0.3101 g, 7.44×10^{-4} mol) and $[(CH_3(CH_2)_3)_4N][HSO_4]$ (20.0 g, 5.71×10^{-2} mol) or $[NaHSO_4]$ (7.87 g, 5.71×10^{-2} mol) was dissolved in 40 cm^3 of water under the following reaction conditions: CO = 20 g (53 atm); $T = 150$°C for 5.7 h. Both Ru/$[(CH_3(CH_2)_3)_4N][HSO_4]$ and Ru/$[NaHSO_4]$ systems catalyzed the WGSR with TOF(CO_2)/24 h values of 185 and 152 observed, respectively. Analyses of both catalytic solutions by GC revealed no formation of organic products. The TOF(CO_2)/24 h value for the Ru/$[(CH_3(CH_2)_3)_4N][HSO_4]$ system is 1.2 times larger than the value for the Ru/$NaHSO_4$ system. Again this may result from enhanced solubility of CO due to the presence of $[(CH_3(CH_2)_3)_4N][HSO_4]$. Further, a control experiment shows Ru complex decomposition and no WGSR activity in the absence of one of the cocatalyst salts under similar reaction conditions. On the other hand, the fact that the Ru/$[(CH_3(CH_2)_3)_4N]^+$ system is more active than Ru/$[Na]^+$ could depend on the better ability of the $[(CH_3(CH_2)_3)_4N]^+$ cation to withdraw electron density from the CO coordinated to Ru. The Na^+ and $[(CH_3(CH_2)_3)_4N]^+$ cations are classified as hard and soft acids, respectively, and CO as a soft base [20]. In the Pearson hard and soft acid and base concept, the soft–soft interaction is more effective than hard–soft [21]. In this case the CO/$[(CH_3(CH_2)_3)_4N]^+$ (soft–soft) interaction is more effective than the CO/Na^+ (soft–hard) interaction. The withdrawal of electron density from coordinated CO by the cation $[(CH_3(CH_2)_3)_4N]^+$ or Na^+ makes the CO more electrophilic and renders the CO susceptible to nucleophilic attack by water, which facilitates the formation of the Ru-hydroxycarbonyl species Ru-CO_2H, a key species formed in the WGSR catalytic cycle, and which leads to product formation, CO_2 and H_2 [3,22].

Further, after cooling the reactor, an orange-yellow solid was isolated from the Ru/$[(CH_3(CH_2)_3)_4N][HSO_4]$ and Ru/$NaHSO_4$ catalytic solutions and identified as $Ru_3(CO)_{12}$. Ford *et al.* [23] reported that a mixture of $Ru_3(CO)_{12}$/KOH/methanol catalyzed the WGSR with a TOF(CO_2)/24 h of 53 observed under the following reaction conditions: $P(CO) = 75$ atm at 135°C. Our Ru/$[(CH_3(CH_2)_3)_4N][HSO_4]$ and Ru/$[NaSO_4]$ systems are 3.5 and 2.9 times, respectively, more active than the $Ru_3(CO)_{12}$/KOH/methanol system. An explanation based on the interaction of the Ru–CO species with the hard K^+ cation can account for the observed differences in catalytic activity of these systems. The hydration enthalpies of the polarizing K^+ and Na^+ cations are -251.2 and -239.7 kJ mol^{-1} at 298 K [24], respectively. Accordingly, the dehydration process is more favorable for Na^+ than K^+. Interaction of the cation with the coordinated CO, which facilitates nucleophilic attack of water, requires a previous dehydration step.

Mechanistic Consideration

Scheme 1 illustrates the proposed mechanisms for hydrocarboxylation of ethylene by the more active mononuclear Ru(II) species. Three independent cycles account for the observed products. In cycle **(I)**, formation of propionic acid implies hydrolysis of Ru–C bonds in the unit Ru–C(O)CH_2CH_3 (Ru–acyl) as one of the termination steps. Nucleophilic attack by water (step a) on the Ru–acyl precursor complex **(1)** leads to formation of propionic acid and a Ru–hydride complex **(2)**. Addition of ethylene to this complex (step b) forms a Ru–ethylene complex, which by further insertion of the coordinated ethylene molecule in the Ru–H bond generates the Ru–alkyl complex **(3)**. Finally, migration of the alkyl group to a coordinated *cis*-CO, assisted by coordination of a CO molecule (step c) leads to the formation of the Ru–acyl complex **(1)** to close catalytic cycle **(I)**. The Lewis-acid promoted migratory-insertion of an alkyl group to a coordinated CO affording an acyl intermediate has been reported [25]. In our systems the presence of Na^+ or $[(CH_3(CH_2)_3)_4N]^+$ Lewis acids should accelerate the formation of this key intermediate, increasing catalytic activity, and because Na^+ is a better Lewis acid than $[(CH_3(CH_2)_3)_4N]^+$, one expects that the Ru/$NaHSO_4$ system should have a greater catalytic activity than the Ru/$[(CH_3(CH_2)_3)_4N]HSO_4$ system. However, the opposite is observed. The answer lies in the more favorable dehydration entropy for the nonpolarizing $[(CH_3(CH_2)_3)_4N]^+$ than for Na^+. Interaction of the cation with the coordinated CO requires that the hydrated cation removes the water



SCHEME 1 Proposed mechanism.

from its coordination sphere. This process is more favorable for the non-polarizing $[(CH_3(CH_2)_3)_4N]^+$ than for Na^+ [24].

In Scheme 1, the CO and H_2O ligands of the intermediate ruthenium complexes and the interaction of the cations of the cocatalyst $[(CH_3(CH_2)_3)_4N]HSO_4$ and $NaHSO_4$ with intermediates are omitted for clarity.

Cycles **(II)** and **(III)** describe the formation of diethyl ketone and propanal which come from *in situ* hydrogenolysis of the Ru–acyl complex. The diethyl ketone may arise from insertion of ethylene to form the intermediate $[Ru\text{-}C_2H_4C(O)C_2H_5]^+$ **(4)**. The $[Ru–C_2H_4C(O)C_2H_5]^+$ species are terminated by reaction with the CO/H_2O couple affording CO_2, the corresponding diethyl ketone (step e) and Ru–H which by CO coordination closes catalytic cycle **(II)**. On the other hand, the hydrogenolysis of the Ru–acyl (**1**) intermediates, which leads to propanal formation (step h), comes probably from *intra*-hydrogen transfer from Ru–H species formed under conditions similar to the WGSR [Eqs. (6) and (7)] [3].

$$[Ru(CO)_2(H_2O)_3(acyl)]^+ + H_2O \rightarrow [Ru(CO)(CO_2H)(H_2O)_3(acyl)] + H^+ \qquad (6)$$

Decarboxylation would generate a ruthenium hydride complex $[HRu(CO)(H_2O)_3$ $(acyl)]$ and CO_2 [Eq. (7)].

$$[Ru(CO)(CO_2H)(H_2O)_3(acyl)] \rightarrow [HRu(CO)(H_2O)_3(acyl)] + CO_2 \qquad (7)$$

Reductive elimination of hydride–acyl affords propanal and the coordinatively unsaturated $[Ru(CO)(H_2O)_3]$ complex according to Eq. (8).

$$[HRu(CO)(H_2O)_3(acyl)] \rightarrow [Ru(CO)(H_2O)_3] + C_2H_5C(O)H \qquad (8)$$

Protonation of the latter neutral complex by H^+ [see Eq. (6)], followed by coordination of ethylene and migratory insertion in the Ru–H bond [26] gives Ru-C_2H_5. Then *cis*-migration of the C_2H_5 group to the Ru-CO moiety assisted by coordination of another CO gives the starting $[Ru(CO)_2(H_2O)_3(acyl)]^+$ complex (**1**) to close catalytic cycle (**III**). The overall reaction is shown in Eq. (9):

$$4C_2H_4+3H_2O + 5CO \rightarrow C_2H_5CO_2H + C_2H_5C(O)C_2H_5+C_2H_5C(O)H + 2CO_2 \quad (9)$$

Further, the TOF/24 h values of propionic acid formation (runs 1–5, Table I) are better than the TOF/24 h values of diethyl ketone and propanal formation (based on CO_2 formed) by a factor of 2.2 to 9.5. These results suggest that the termination step by hydrolysis affording propionic acid is faster than the termination steps by hydrogenolysis affording diethyl ketone and propanal. These results also suggest that step (a) involving the hydrolysis of the Ru-acyl complex **(1)** is not the rate-determining step.

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References

[1] J.W. Reppe and E. Reindl, *Leibigs Ann. Chem.* **582**, 121 (1953).
[2] H. Kang, C.H. Mauldin, T. Cole, W. Slegeir, K. Cann and R. Pettit, *J. Am. Chem. Soc.* **99**, 8323 (1977).
[3] P.C. Ford and A. Rokicki, *Adv. Organometal. Chem.* **28**, 139 (1988).
[4] T. Welton, *Chem. Rev.* **99**, 201 (1999).
[5] J. Holbrey and K.R. Seddon, *Clean Prod. Proc.* **1**, 223 (1999).
[6] K.R. Seddon, *J. Chem. Tech. Biotech.* **68**, 351 (1997).
[7] P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed. Engl.* **39**, 3773 (2000).
[8] K. Weissermel and H.J. Harpe, Industrial Organic Chemistry (VCH, Weinheim, 1993).
[9] P. Pino, F. Piacenti F and M. Bianchi, In: I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls (John Wiley & Sons, New York, 1968) 233 pp.
[10] M. Kilner and N.J. Winter, *J. Mol. Catal. A* **112**, 327 (1996).
[11] A. Cabrera, P. Sharma, J.L. Garcia, L. Velazco, F.J. Perez, J.L. Arias and N. Rosas, *J. Mol. Catal. A* **118**, 167 (1997).
[12] G. Verspui, J. Feiken, G. Papadogianaskis and R.A. Sheldon, *J. Mol. Catal. A* **146**, 299 (1999).
[13] T. Funaioli, C. Cavazza, F. Marchetti and G. Fachinetti, *Inorg. Chem.* **38** 3361 (1999).
[14] Y. Iwashita and M. Sakuraba, *Tetrahedron Lett.* **26**, 2409 (1971).
[15] P. Hong and H. Yamazaki, *Chem. Lett.* 1335 (1979).
[16] P. Hong, and H. Yamazaki, *J. Mol. Catal.* **26**, 297 (1984).
[17] A. Sen and J.S. Brumbaugh, *J. Organometal. Chem.* **279**, C5 (1985).
[18] C. Starks, C. Liotta and M. Halpern, Phase Transfer Catalysis: Fundamentals, Applications and Industrial Perspective (Chapman & Hall, New York, 1994).
[19] R.M. Laine, *J. Mol. Catal.* **14**, 137 (1982).
[20] R.G. Pearson, *J. Chem. Ed.* 64, 561 (1987).
[21] R.G. Pearson, Chemical Hardness (Wiley-VCH, Weinheim, 1999).
[22] P. Aguirre, R. López, D. Villagra, I. Azocar-Guzman, A.J. Pardey and S.A. Moya, *Appl. Organomet. Chem.* **17**, 36 (2003).
[23] P.C. Ford, C. Ungermann, V. Landis, R.G. Rinker and R. Laine, *Adv. Chem. Ser.* **173**, 81 (1979).
[24] W.E. Dasent, Inorganic Energetics (Penguin Books, Glasgow,1970).
[25] S.B. Butts, E.M. Holt, S.H. Strauss, N.W. Alcock, R.E. Stimson and D.F. Shriver, *J. Am. Chem. Soc.* **101**, 5864 (1979).
[26] G. Consiglio, *Chimia*, **55**, 809 (2001).