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Mechanism and selectivity control of methyl acetate and methyl formate formation from methanol alone with $[Ru(SnCl_3)_5(PPh_3)]^{3-}$ as catalyst †

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Mechanistic studies have been made of the unique one-pot conversion of methanol into acetic acid (and/or methyl acetate due to rapid esterification) with $[Ru(SnCl_3)_5(PPh_3)]^{3-}$ as catalyst. Addition of Cl^- ion promoted the formation of methyl formate relative to methyl acetate, but scarcely changed their total rate of formation. Further, the activation energies for their formation were virtually identical ($\approx$76 kJ mol^{-1}). No ^{13}C was incorporated into methyl acetate even when the reaction was performed under a ^{13}CO atmosphere, indicating that the conversion of methanol into methyl acetate does not involve carbonylation. The effect of the addition of Cl^- ion on the reaction of formaldehyde was similar to that when using methanol as substrate, but quite different activation energies were obtained for the formation of methyl acetate (27.9 kJ mol^{-1}) and methyl formate (40.6 kJ mol^{-1}). The results are in accord with rate-determining dehydrogenation of methanol to formaldehyde (as a common intermediate), which is then converted competitively into acetic acid and methyl formate with different activation energies. The effect of added free Cl^- ion for both substrates suggests the presence of a pre-equilibrium dissociation of Cl^- from the co-ordinated $SnCl_3^-$, which is required for the formation of acetic acid but not for methyl formate. A possible reaction scheme is presented, in which reductive elimination of methyl formate is competitive with that of acetic acid.

We have previously reported the unprecedented reaction in which acetic acid (and/or methyl acetate due to rapid esterification) is formed from methanol alone with the ruthenium(II)–tin(II) complexes $[Ru(SnCl_3)_5L]^{3-}$ ($L = PPh_3$ **1** or MeCN **2**) used as homogeneous catalysts.[2] Comparison of the catalytic activities among a series of ruthenium(II) complexes $[RuCl_2\{P(OMe)_3\}_4]$ **3**, $[RuCl(SnCl_3)\{P(OMe)_3\}_4]$ **4** and $[Ru(SnCl_3)_2\{P(OMe)_3\}_3]$ **5** for methanol and possible intermediates[2] in the overall reaction [formaldehyde (formed as paraformaldehyde) and methyl formate] revealed that only **5** could catalyse the conversion of methanol into acetic acid, which also converted paraformaldehyde or methyl formate into acetic acid.[3] Complex **3** showed merely a catalytic activity for the Tischenko-type dimerisation ($2HCHO \longrightarrow HCO_2Me$), and **4** exhibited an intermediate character, being able to catalyse the two reactions ($2HCHO \longrightarrow HCO_2Me$ and $HCO_2Me \longrightarrow MeCO_2H$) but unable to react with methanol. Thus the unique character of the $SnCl_3^-$ ligand is obvious.

When complex **1** is used as catalyst we have preliminarily observed that the selectivity for methyl acetate *vs.* methyl formate formation can be varied systematically by the amount of extra Cl^- ion added. We have now investigated the mechanism of this unique conversion of methanol in detail with **1** used as catalyst.

Results

A representative time course for selective conversion of methanol into methyl acetate with **1** as catalyst is shown in Fig. 1. The turnover number is calculated as the amount of product (mol) divided by the amount of complex charged (mol). Methyl formate was formed in trace amount, and methyl acetate would be formed from acetic acid by rapid esterification with the methanol present in excess as a substrate.[1–5] For kinetic studies, reactions were performed at a lower temperature (65 °C), and initial rates were determined from the initial linear slopes of the time *vs.* conversion curves. During this period the UV/VIS spectrum of the reaction solution exhibited no appreciable change, showing a single peak with $\lambda_{max} = 360$ nm; however this peak changed into a broad peak with a shoulder at 430 nm when the catalytic activity was lowered considerably. Virtually stoichiometric formation of dihydrogen and methyl acetate was ensured (within 5% error).

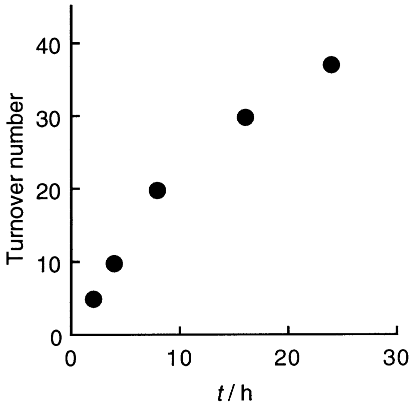

Fig. 1 Time course for the conversion of methanol (0.025 mol) into methyl acetate with $[Ru(SnCl_3)_5(PPh_3)]^{3-}$ as catalyst (1.00×10^{-7} mol), nitromethane solvent (1.0 cm^3) at 140 °C. The reaction was performed in a glass ampoule (7.0 cm^3) sealed under vacuum with the solution frozen by liquid nitrogen

Dependence on the catalyst concentration

The catalyst concentration was varied between 2.50×10^{-5} and 1.00×10^{-4} mol dm^{-3}, with the substrate maintained at 12.5 mol dm^{-3}. The rate dependence on the catalyst concentration (Fig. 2) clearly shows that the rate is first order with respect to the catalyst concentration.

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† Synthesis of acetic acid from methanol alone by homogeneous metal complex catalyst. Part 3.[1]
Non-SI unit employed: atm = 101 325 Pa.

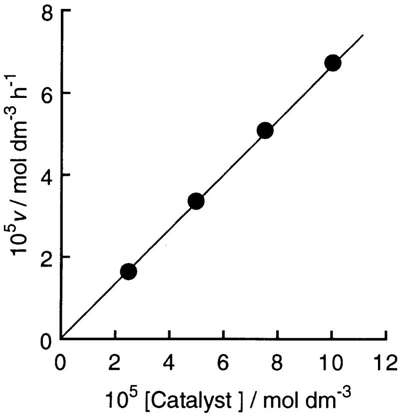


Fig. 2 Initial rate of formation of methyl acetate as a function of the catalyst concentration. Methanol 2.5 mol, solvent (nitromethane) 100 cm^3, under N_2 (1 atm), 65 °C

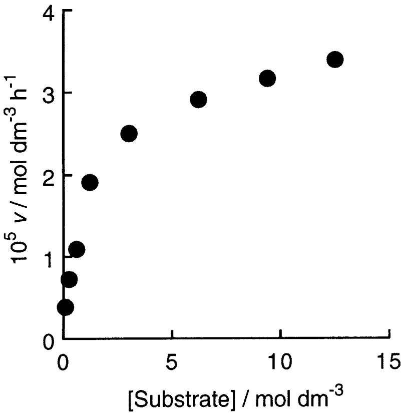


Fig. 3 Initial rate of formation of methyl acetate as a function of substrate concentration (methanol). Catalyst, $[Ru(SnCl_3)_5(PPh_3)]^{3-}$, 1.00 × 10^{-5} mol, solution volume 200 cm^3 (nitromethane solvent), under N_2 (1 atm), 65 °C

Dependence on the substrate concentration

The substrate concentration was varied between 0.125 and 12.5 mol dm^{-3} at the constant catalyst concentration of 5.0 × 10^{-5} mol dm^{-3}. As shown in Fig. 3, the rate of methyl acetate formation showed saturation at high concentrations.

Effect of extra addition of free Cl^-

Free Cl^- ion was added as NEt_4Cl in the concentration range 1.5 × 10^{-5}–3.5 × 10^{-5} mol dm^{-3}, the ionic strength of the solution (I) being kept constant with NEt_4ClO_4. Notably, as revealed in Fig. 4, the addition of free Cl^- strongly affected the product selectivity. While methyl acetate is a main product without NEt_4Cl [Fig. 4(*a*)], addition of NEt_4Cl makes the formation of methyl formate predominant with a concomitant decrease in methyl acetate [Fig. 4(*b*)]. Fig. 5 shows the effect of changing the added amount of Cl^- ion on the relative rate of methyl acetate and methyl formate formation; the formation of methyl formate became faster than that of methyl acetate at about 3.5 × 10^{-5} mol dm^{-3} ($[Cl^-]_{ad}/[Ru]_0 = 0.7$). Despite the observed drastic change in product selectivity, the addition of free Cl^- ion scarcely changed the total rate of formation for methyl acetate and methyl formate throughout the concentration range examined (*cf.* Fig. 4).

Effect of extra addition of free PPh_3

Interestingly the extra addition of PPh_3 ($[PPh_3]_{ad}$ = 2.5 × 10^{-5}–2.5 × 10^{-4} mol dm^{-3}) not only affected the product selectivity but also lowered the total rate of formation for the two products (Fig. 6). The ratio of the associated rates is given as a function of $[PPh_3]_{ad}$ in Fig. 7. When the reciprocal of the total rate is plotted as a function of $[PPh_3]_{ad}$, an almost linear dependence is obtained although a slight upward deviation appears at low concentration (Fig. 8).

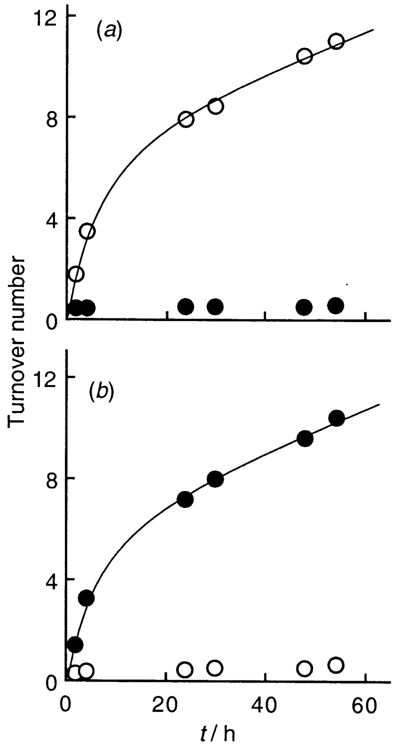


Fig. 4 Effect of the addition of Cl^- ion on the conversion of methanol into methyl acetate (○) and methyl formate (●) with $[Ru(SnCl_3)_5(PPh_3)]^{3-}$ as catalyst (1.00 × 10^{-5} mol). Methanol 2.5 mol, solvent (nitromethane) 100 cm^3, under N_2 (1 atm), 65 °C. (*a*) NEt_4ClO_4 7.50 × 10^{-5} mol dm^{-3}, (*b*) NEt_4Cl 5.00 × 10^{-5} mol dm^{-3}, NEt_4ClO_4 2.50 × 10^{-5} mol dm^{-3}

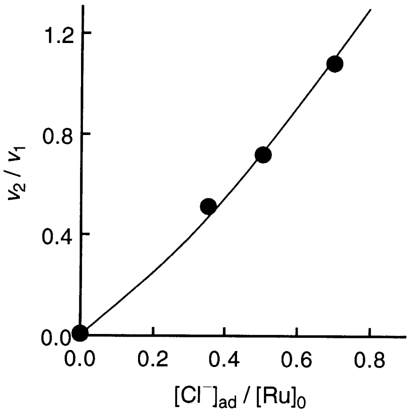


Fig. 5 Dependence of the ratio of the initial rates for the formation of methyl acetate (v_1) and methyl formate (v_2) on the amount of Cl^- added. Catalyst, $[Ru(SnCl_3)_5(PPh_3)]^{3-}$, 1.00 × 10^{-5} mol, methanol 2.5 mol, solvent (nitromethane) 100 cm^3, under N_2 (1 atm), I = 3.75 × 10^{-4} mol dm^{-3}, 65 °C

Reactions under CO and ^{13}CO atmospheres

When the reaction was performed under a CO atmosphere (1 atm) the product selectivity (exclusively methyl acetate) was unchanged, but the rate of methyl acetate formation was reduced to *ca.* $\frac{1}{3}$. Hence the presence of CO molecules in the solution diminishes the reaction rate. It was further found that even when the reaction was performed under a ^{13}CO atmosphere no ^{13}C was incorporated into the methyl acetate formed; the mole ratio of methyl acetate formed to ^{13}CO charged was

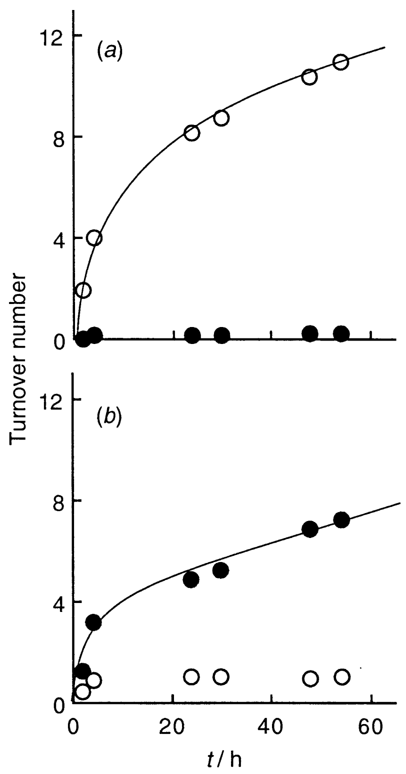


Fig. 6 Effect of the addition of PPh_3 on the conversion of methanol into methyl acetate (○) and methyl formate (●) with $[Ru(SnCl_3)_5(PPh_3)]^{3-}$ as catalyst (1.00×10^{-5} mol). Methanol 2.5 mol, solvent (nitromethane) 100 cm^3, under N_2 (1 atm), 65 °C. (*a*) No addendum, (*b*) $[PPh_3]_{ad} = 1.50 \times 10^{-4}$ mol dm^{-3}

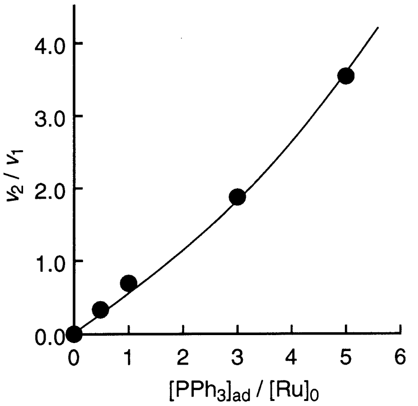


Fig. 7 Dependence of the ratio of the initial rates for the formation of methyl acetate (v_1) and methyl formate (v_2) on the amount of PPh_3 added. Catalyst, $[Ru(SnCl_3)_5(PPh_3)]^{3-}$, 1.00×10^{-5} mol, methanol 2.5 mol, solvent (nitromethane) 100 cm^3, under N_2 (1 atm), 65 °C

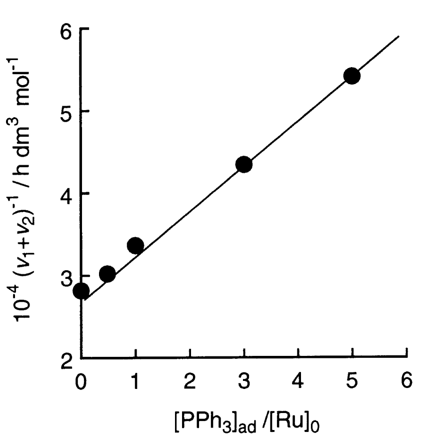


Fig. 8 Reciprocal of the initial rate of formation of methyl acetate and methyl formate (total) plotted as a function of the amount of PPh_3 added. Conditions as in Fig. 7

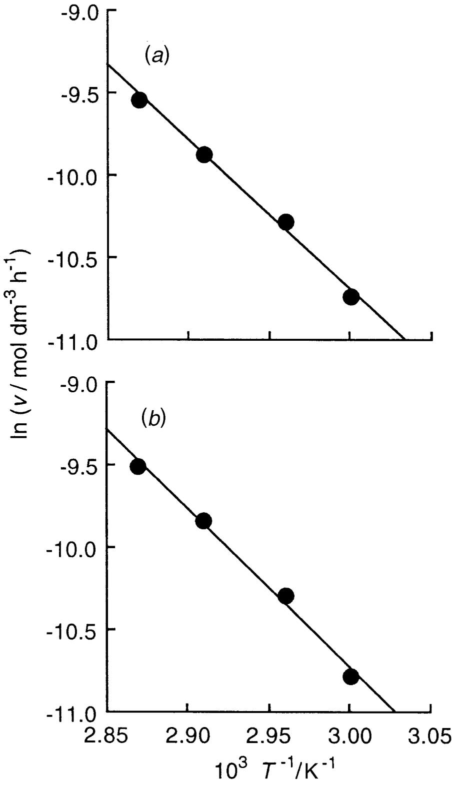


Fig. 9 Temperature dependence of the initial rates for the formation of methyl acetate (*a*) and methyl formate (*b*). Catalyst, $[Ru(SnCl_3)_5(PPh_3)]^{3-}$, 1.00×10^{-5} mol, $[Cl^-]_{ad} = 0$ (*a*) and 5.00×10^{-5} mol dm^{-3} (*b*), $I = 3.75 \times 10^{-4}$ mol dm^{-3}, methanol 2.5 mol, solvent (nitromethane) 100 cm^3, under N_2 (1 atm)

sufficiently small (3.5%), and the mass spectral patterns, *m*/*z* 74 ($Me^{12}CO_2Me$) and 75 ($Me^{13}CO_2Me$), for the methyl acetate formed under ^{12}CO and ^{13}CO atmospheres commonly showed an intensity ratio [*I*(*m*/*z* 75)/*I*(*m*/*z* 74)] identical to the value (3.5%) calculated for the natural abundance of ^{13}C.

Dependence on the partial pressure of H_2

The reaction was performed by varying the partial pressure of H_2 at a total pressure of 1 atm (N_2 + H_2). Under these conditions methyl acetate was still formed exclusively at a virtually constant rate.

Activation energy

The temperature dependence of the rate of methyl acetate formation is shown in Fig. 9(*a*) in the form of an Arrhenius plot. From the slope of the straight line (correlation coefficient = 0.995) an activation energy of 75.7 kJ mol^{-1} was obtained.

When the temperature dependence was examined in the presence of added Cl^- ion ($[Cl^-]_{ad}/[Ru]_0 = 1$), where methyl formate was selectively formed, an activation energy of 76.3 kJ mol^{-1} was obtained for methyl formate formation [Fig. 9(*b*), correlation coefficient = 0.998]. Thus the activation energies for methyl acetate and methyl formate are virtually identical, when the respective correlation coefficients are taken into account.

Reaction with formaldehyde

It was suggested that formaldehyde was formed in the first step of conversion of methanol into both acetic acid and methyl formate as a common intermediate.[3] Therefore we performed the reaction of formaldehyde (*i.e.* paraformaldehyde as a formaldehyde precursor) with the present catalyst. Interestingly the effect of extra addition of free Cl^- is quite similar to that in

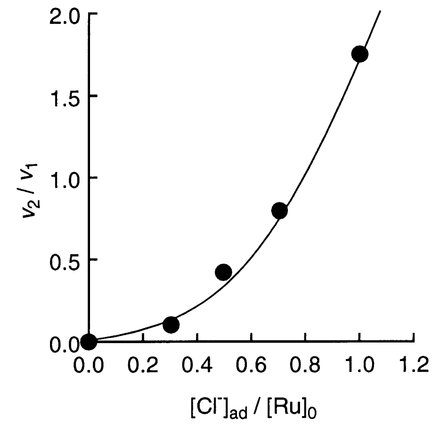


Fig. 10 Dependence of the ratio of the initial rates for the formation of methyl acetate (v_1) and methyl formate (v_2) on the amount of Cl^- added. Catalyst, $[Ru(SnCl_3)_5(PPh_3)]^{3-}$, 1.00×10^{-5} mol, paraformaldehyde equivalent to 1.25×10^{-2} mol formaldehyde, solvent (nitromethane) 100 cm^3, under N_2 (1 atm), $I = 7.50 \times 10^{-4}$ mol dm^{-3}, 65 °C

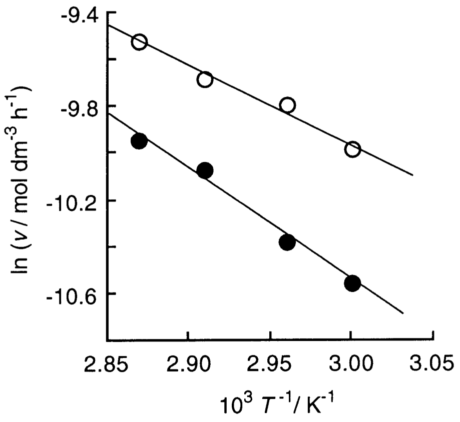


Fig. 11 Temperature dependence of the initial rates for the formation of methyl acetate (○) and methyl formate (●). Catalyst, $[Ru(SnCl_3)_5(PPh_3)]^{3-}$, 1.00×10^{-5} mol, $[Cl^-]_{ad} = 0$ (○) and 1.50×10^{-4} mol dm^{-3} (●), $I = 7.50 \times 10^{-4}$ mol dm^{-3}, paraformaldehyde equivalent to 1.25×10^{-2} mol formaldehyde, solvent (nitromethane) 100 cm^3, under N_2 (1 atm)

the case of methanol as substrate; while methyl acetate and acetic acid were exclusively formed without added NEt_4Cl, addition of NEt_4Cl made the formation of methyl formate appreciable (Fig. 10). The initial rates for the two products are almost the same at $[Cl^-]_{ad}/[Ru]_0 = 0.8$, and the formation of methyl formate became predominant above $[Cl^-]_{ad}/[Ru]_0 = 1.3$. From the temperature dependences of the reaction rate determined with $[Cl^-]_{ad}/[Ru]_0 = 0$ and 1.5, activation energies of 27.9 and 40.6 kJ mol^{-1} were obtained for the formation of methyl acetate (+ acetic acid) and methyl formate, respectively (Fig. 11).

Discussion

No incorporation of ^{13}C into the product methyl acetate in the experiment with ^{13}CO evidently indicates that the conversion of methanol into methyl acetate does not involve any process of carbonylation. The rate retardation on changing the reaction atmosphere from N_2 to CO is due to the inhibitive co-ordination of CO to the catalytic site. These results support the previous postulation[3] that the reaction involves the initial dehydrogenation of methanol to formaldehyde which is then converted into methyl formate or acetic acid.

Since (*i*) the activation energies for methyl acetate and methyl formate formation from methanol were virtually identical (Fig. 9), and (*ii*) the total rate of their formation was hardly changed upon extra addition of free Cl^- ion over a wide concentration range (*cf.* Fig. 4), it seems reasonable to postulate that the initial dehydrogenation step to produce formaldehyde (either free or co-ordinated[6]) is rate determining, which would be converted relatively rapidly into either of the two final products. Since the rate of methanol conversion is independent of the partial pressure of H_2, the dehydrogenation step should be irreversible (not an equilibrium), which strongly supports the postulation above.

As the effect of added free Cl^- ion on the total rate of methanol conversion was very small, it is feasible that the rate-determining step to produce formaldehyde does not include any equilibrium dissociation of Cl^-. The processes after the rate-determining step may competitively produce methyl formate and acetic acid, and their relative contribution would be affected by the presence of free Cl^- ion (see below).

Since the total rate to form the two products is diminished upon the addition of free PPh_3 (Fig. 6), the presence of a pre-equilibrium dissociation of PPh_3 ligand from the catalyst is indicated as in equation (1). If the intermediate formed gives

$$[Ru(SnCl_3)_5(PPh_3)]^{3-} + MeOH \overset{K}{\rightleftharpoons} [Ru(SnCl_3)_5(MeOH)]^{3-} + PPh_3 \quad (1)$$

the product (formaldehyde) with a first-order rate constant k, the overall rate can be expressed as in equation (2) where

$$v = kK[Ru]_0[MeOH]/(K[MeOH] + [PPh_3]) \quad (2)$$

$[Ru]_0$ is the concentration of catalyst charged. The linear correlation between v and $[Ru]_0$ (Fig. 2), and the saturation curve for v *vs.* [MeOH] (Fig. 3) are both consistent with this equation. Equation (2) can be rearranged to give (3). This equation

$$\frac{1}{v} = \frac{1}{k[Ru]_0} + \frac{[PPh_3]}{kK[Ru]_0[MeOH]} \quad (3)$$

accounts for the linear relationship between $1/v$ and $[PPh_3]_{ad}$ (Fig. 8). The upward deviation in the low-concentration region is due to the inherent contribution of ligand dissociation to the total concentration of the free phosphine, which should become appreciable in this region. The values of k and K obtained from the slope and intercept are 0.71 h^{-1} and 2.2×10^{-5}, respectively. As the extra addition of PPh_3 affected the product selectivity (Figs. 6 and 7), co-ordination of PPh_3 to the tin(II) site[7] should be taken into account (see below). However, since the additive effect is relatively small and requires a large amount of PPh_3 (in comparison to the case of Cl^-), the effect of co-ordination may be neglected when equation (1) is considered. It is to be noted that catalytic dehydrogenation of methanol to produce formaldehyde (+ formaldehyde dimethyl acetal) and/or methyl formate is possible with simple ruthenium(II) complexes without $SnCl_3^-$ as ligand.[8–10] Therefore, $SnCl_3^-$ would act merely as an auxiliary ligand in this dehydrogenation process.

It has definitely been shown that extra addition of Cl^- blocks the reaction path for acetic acid formation not only for the methanol substrate (Figs. 4 and 5) but also for the formaldehyde substrate (Fig. 10) in a similar way. This fact may also support the intermediacy of formaldehyde in the overall reaction. This blocking effect can be explained in terms of an equilibrium dissociation of Cl^- from the co-ordinated $SnCl_3^-$, which is required for the formation of acetic acid but not for methyl formate. Since the dehydrogenation step to form formaldehyde is considered to be rate determining, a rather large difference in the activation energy observed when formaldehyde is used as substrate (Fig. 11) is associated with the competitive processes after the rate-determining step. The smaller magnitude of these activation energies compared to that for methanol as substrate (≈76 kJ mol^{-1}) may be consistent with this view. The higher activation energy for methyl formate formation

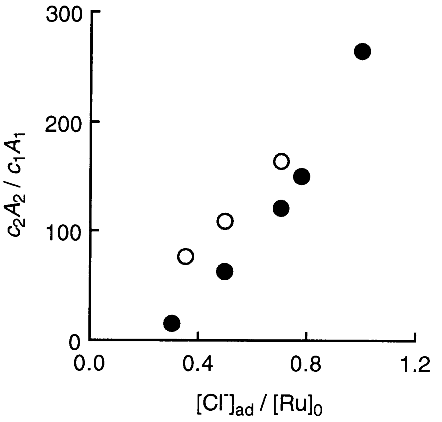


Fig. 12 Dependence of c_2A_2/c_1A_1 for methanol (○) and paraformaldehyde (●) substrates [*cf.* equation (4) in the text] on the amount of Cl^- added. Reaction conditions as in the captions of Figs. 5 and 10, respectively

(40.6 kJ mol^{-1}) suggests that this process is energetically disfavoured, even if it can proceed with Cl^- retained in the co-ordinated $SnCl_3^-$. Thus, without the blocking effect of added Cl^- ion, methyl acetate should be formed preferably with a lower activation energy (27.9 kJ mol^{-1}) accompanying chloride dissociation.

Equation (4) may be deduced if the rate is first order with

$$\nu_2/\nu_1 = [c_2A_2 \exp(-E_{a_2}/RT)]/[c_1A_1 \exp(-E_{a_1}/RT)] \quad (4)$$

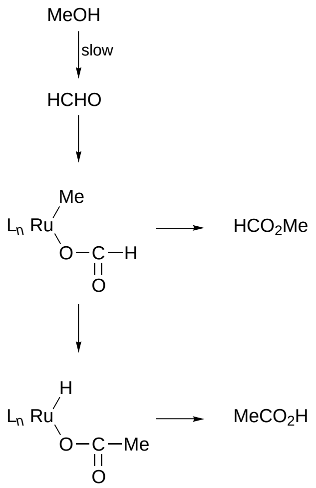
respect to the concentration of catalytically active species, where ν_1 and ν_2 are the rates of formation of methyl acetate and methyl formate, respectively, c_1 is the concentration of the species lacking Cl^-, and c_2 that of the species retaining Cl^-. In the case of $\nu_2/\nu_1 = 1$ ($[Cl^-]_{ad}/[Ru]_0 = 0.78$, Fig. 10), for instance, equation (5) is obtained. Substitution with the observed E_a

$$(c_2A_2)/(c_1A_1) = \exp[-(E_{a_1} - E_{a_2})/RT] \quad (5)$$

values and T (338.15 K) yields 151 for $(c_2A_2)/(c_1A_1)$. Fig. 12 (solid circles) shows a plot of this ratio {calculated from $(\nu_2/\nu_1)\exp[-(E_{a_1} - E_{a_2})/RT]$} as a function of $[Cl^-]_{ad}/[Ru]_0$. The open circles correspond to the values estimated using ν values for methanol as substrate and E_a values for formaldehyde as substrate. Based on the assumption of the common intermediacy of formaldehyde, the two plots should be close to each other. This seems to hold fairly well, and one of the reasons for the small discrepancy may be the difference in reaction medium [paraformaldehyde dissolved in nitromethane *vs.* nitromethane–methanol (1:1, v/v)].

On a thermodynamic basis, acetic acid is preferred to methyl formate as a dehydrogenation product of methanol,[11] *e.g.* at 25 °C: $2MeOH(g) \longrightarrow MeCO_2H(g) + 2H_2$, $\Delta H° = -32.5$ kJ mol^{-1}, $\Delta G° = -51.7$ kJ mol^{-1}; $2MeOH(g) \longrightarrow HCO_2Me(g) + 2H_2$, $\Delta H° = 52.6$ kJ mol^{-1}, $\Delta G° = 27.8$ kJ mol^{-1}. Therefore, if an appropriate catalyst is provided, acetic acid can be formed more easily than methyl formate. Further, the $\Delta G°$ values suggest that a rather high temperature is necessary to obtain a high equilibrium conversion for methyl formate, but room temperature is enough for acetic acid.

A possible reaction path is shown in Scheme 1, which represents the competitive formation of acetic acid and methyl formate after the rate-determining step. This scheme is based[3] on the grounds that a methyl(formato) complex is formed from formaldehyde, which then gives methyl formate upon reductive elimination,[12] and that the methyl(formato) complex could be isomerised into a hydridoacetato complex and give acetic acid upon reductive elimination.[13] Usually a hydride complex is thermodynamically more stable than the corresponding methyl complex.[14] This may be a driving force for the relevant isomerisation process, since the substituent effect on the carboxylate group (H or Me) would be weaker than the steric (and/or electronic) effect of the respective ligands.



Scheme 1 Competitive formation of methyl formate and acetic acid from methanol alone *via* the methyl(formato) and hydridoacetato complexes, respectively

The observed product selectivity strongly suggests that the vacant site on Sn^{II} formed upon releasing a Cl^- ligand promotes the isomerisation step in Scheme 1. In view of the bimetallic nature of the catalytic site, the promotion effect may operate possibly through the formation of μ-carboxylate-type bridging[15] and/or the stabilisation of a CO_2-co-ordinated intermediate.[13]

Conclusion

It is demonstrated that the selectivity for the conversion of methanol using complex **1** as catalyst can be controlled systematically by extra addition of free Cl^- or PPh_3. Although such addition enhanced the formation of methyl formate relative to methyl acetate, the total rate of methanol conversion was not changed with Cl^- but was reduced considerably by PPh_3. The activation energies for the formation of methyl acetate and methyl formate, obtained under different conditions of $[Cl^-]_{ad}$, are virtually identical, which suggests the presence of a common intermediate, the formation of which is rate determining for the two final products.

No incorporation of ^{13}C into methyl acetate in the experiment with ^{13}CO indicates the lack of a carbonylation process in its formation. A similar dependence on $[Cl^-]_{ad}$ for the formation of methyl acetate (+ acetic acid) and methyl formate with formaldehyde as substrate strongly suggests that formaldehyde is the presumed intermediate, the formation of which is rate determining. The invariance of the rate of reaction on the partial pressure of H_2 supports this view.

After its rate-determining formation, formaldehyde would then be converted competitively into methyl acetate and methyl formate. The former process is energetically favoured ($E_a = 27.9$ kJ mol^{-1}), but would require pre-equilibrium dissociation of Cl^- from the co-ordinated $SnCl_3^-$. The latter process, on the other hand, is energetically difficult ($E_a = 40.6$ kJ mol^{-1}), but would proceed with retention of Cl^-. On these grounds, a selectivity factor, $(c_2A_2)/(c_1A_1)$, was evaluated for both methanol and formaldehyde as substrate with various values of $[Cl^-]_{ad}$ (c = concentration of catalytically active species, A = pre-exponential factor for Arrhenius equation).

Kinetic analysis of the rate retardation upon addition of free PPh_3 indicates a pre-equilibrium dissociation of PPh_3 ligand in the conversion of methanol into formaldehyde. In this step as well as in the conversion of formaldehyde into methyl formate, $SnCl_3^-$ would simply act as an auxiliary ligand.

A possible reaction scheme is presented for the competitive formation of methyl acetate and methyl formate from formaldehyde. The vacant site on Sn^{II} formed by release of a Cl^- ligand would promote the formation of μ-carboxylate-type bridging and/or stabilise the CO_2-co-ordinated intermediate to enhance the selectivity to acetic acid.

Experimental

The complex $[Ru(SnCl_3)_5(PPh_3)]^{3-}$ was synthesized as reported previously.[16] All chemicals were of reagent grade. Methanol was dried over CaH_2 and then Na, and distilled immediately before use. Nitromethane was dried over $CaSO_4$. Carbon-13 monoxide (99 atom % ^{13}C) was obtained from Merck Frosst Canada Inc. All manipulations were carried out under an argon atmosphere using standard vacuum-manifold and Schlenk techniques.

Typically the reaction solution was prepared by dissolving $[NEt_4]_3[Ru(SnCl_3)_5(PPh_3)]$ (18.8 mg, 1.00×10^{-5} mol) and methanol (100 cm^3, 2.5 mol) in nitromethane solvent (100 cm^3). Unless otherwise stated, the reaction was carried out under a dinitrogen atmosphere (1 atm) at 65 °C. The reactor was equipped with a reflux condenser to which a gas burette with a mercury seal[17] was attached. For precise volumetric measurements, the reaction was performed in a thermostatted room, and the gas burrette was placed in a thermostatted box (±0.2 °C). The products were identified by gas chromatography–mass spectrometry (VG Analytical Autospec-Q) using a 30 m DB-WAX capillary column (inside diameter 0.25 mm), and were analysed quantitatively by gas chromatography (PEG-6000 column).

Acknowledgements

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