



The effect of Mo(CO)₆ as a co-catalyst in the carbonylation of methanol to methyl formate catalyzed by potassium methoxide under CO, syngas and H₂ atmospheres. HP-IR observation of the methoxycarbonyl intermediate of Mo(CO)₆

Samuel Jali^a, Holger B. Friedrich^{a,*}, Gerrit R. Julius^b

^a School of Chemistry, University of KwaZulu-Natal, Westville Campus, Private Bag X 54001, Durban 4000, South Africa

^b Sasol Technology R & D, 1 Klasie Havenga Street, Sasolburg 1947, South Africa

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ABSTRACT

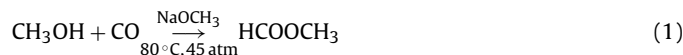
The homogeneous production of methyl formate from methanol, syngas, CO and H₂ co-catalyzed by Mo(CO)₆ in the presence of an alkali methoxide (KOCH₃) is reported. A slight increase in the amount of methyl formate produced by the mixture of Mo(CO)₆/KOCH₃ over the alkali methoxide (KOCH₃) alone, is probably due to the electrophilic nature of Mo-coordinated carbon monoxide compared to free carbon monoxide. The mechanism proposed for the production of methyl formate proceeds *via* a methoxycarbonyl intermediate ([Mo(CO)₅(COOCH₃)]⁻), which is then protonated by methanol to eliminate methyl formate. The methoxycarbonyl adduct was shown to play an important role in the formation of methyl formate from the Mo(CO)₆/KOCH₃ system. The role of this intermediate in the catalytic synthesis of methyl formate from Mo(CO)₆/KOCH₃/CO/MeOH, Mo(CO)₆/KOCH₃/syngas/MeOH, Mo(CO)₆/KOCH₃/H₂/MeOH and Mo(CO)₆/KOCH₃/N₂/MeOH is discussed. HP-IR experiments under H₂ and N₂ atmospheres clearly showed the formation of μ-HMo₂(CO)₁₀⁻ as the methoxycarbonyl intermediate diminishes. The significant role of methanol in the protonation of the methoxycarbonyl adduct is also discussed, as is the effect of polar aprotic solvents such as tetrahydrofuran (THF) and triethylene glycol dimethyl ether (triglyme) in the catalytic synthesis of methyl formate under CO, H₂ and syngas. The amount of methyl formate that is formed is solvent dependent, with methanol showing the highest yield. The stoichiometric effect of Mo(CO)₆ to KOCH₃ in the production of methyl formate is also reported.

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1. Introduction

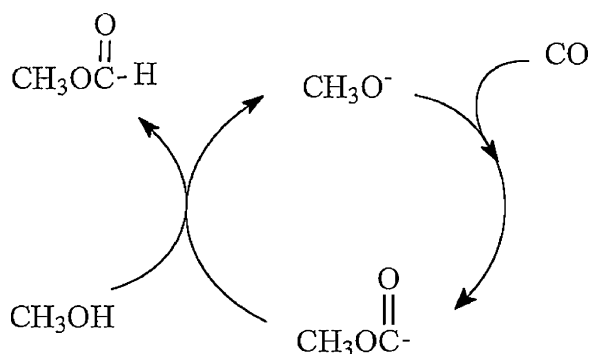
Early studies of carbonylation reactions date back to the time when Reppe discovered that the reaction of CO with methanol produced acetic acid when catalyzed by metal carbonyl compounds of Fe, Co, and Ni in the presence of iodide promoters at 210 °C and 7500 psi of CO [1]. Typical products of carbonylation include methyl formate, methyl acetate, acetic anhydride and acetaldehyde [2,3]. Methyl formate is among the most important industrial products, since it offers an alternative approach to the production of basic chemicals such as acetic acid, acetaldehyde and ethanol [4–6]. Other products of importance from methyl formate are formic acid, dimethyl formamide and ethylene glycol [7,8]. Methyl formate can also react with olefins or halogenated compounds to give esters *via* hydroesterification or alkoxy carbonylation reactions [9,10].

Although methyl formate can be produced from a variety of catalytic processes, the commercial process remains the carbonylation of methanol catalyzed by sodium methoxide (Eq. (1)) at 80 °C and 4.56 MPa of CO, patented by BASF in 1925 [11].



The process involves the nucleophilic attack of the methoxide on carbon monoxide to form a methoxycarbonyl anion (CH₃COO⁻); subsequent protonation of the methoxycarbonyl anion by a methanol molecule produces methyl formate and regenerates the methoxide catalyst (Scheme 1). The disadvantage of this process is that it requires strictly anhydrous conditions as sodium methoxide can be easily hydrolyzed to form methanol and sodium hydroxide, which inhibit the reaction. Sodium hydroxide also reacts with methyl formate to form undesirable products such as sodium formate (HCOONa) [12]. The purity of CO utilized is also critical as the presence of small amounts of CO₂ can result in the deactivation of the catalyst through the formation of insoluble sodium methyl

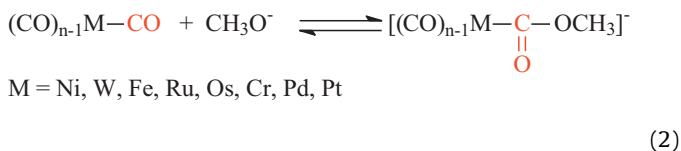
* Corresponding author. Tel.: +27 31 2603107; fax: +27 31 2603091.
E-mail address: friedric@ukzn.ac.za (H.B. Friedrich).



Scheme 1. Methanol carbonylation to methyl formate catalyzed by KOCH_3 .

carbonate (CH_3OCONa) [13,14]. Therefore, a need remains for a more robust catalytic process [8,13].

Studies have shown that addition of a group 6 and/or 8 metal carbonyl to the methoxide process enhances the production of methyl formate and promotes the suppression of trace water impurities formed through the water–gas shift reaction (WGS) [7,15–18]. The rate determining step in the methoxide catalyzed reaction is the attack of the methoxide on the carbon monoxide [7], and addition of group 6 metal carbonyls increases the activity of the catalyst significantly [7,17]. This is probably because the metal carbonyl provides a more electrophilic source of coordinated carbon monoxide, which is nucleophilically attacked by the methoxide anion faster than the free CO, Eq. (2) [15,19–23]. The methoxide anion thus activates the metal coordinated CO to form a short lived methoxycarbonyl (metalloester) complex (Eq. (2)).



At elevated temperature ($T \geq 100^\circ\text{C}$) the metalloester is reported to be protonated by an alcohol in the system, to eliminate methyl formate and regenerate the methoxide. Crucial to mention is that the metal carbonyl is also regenerated under CO atmosphere.

Group 6 metal carbonyls (preferably $\text{Mo}(\text{CO})_6$) were also claimed by Mahajan et al. [23] to enhance the activity of the $\text{Ni}(\text{CO})_4/\text{KOCH}_3$ system in the production of methanol under mild conditions. Ohyama et al. [24] undertook a similar study and examined the individual role played by the claimed metal carbonyls [$\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$] in methanol production. It was revealed that all metal carbonyls without methoxide show low activity in the formation of methyl formate (Cr and W) and dimethyl ether (Mo and Ni), confirming that metal carbonyls alone display little catalytic activity under the claimed conditions. The presence of methoxide enhanced the activity of these metal carbonyls (group 6) and produced a significant amount of methyl formate and dimethyl ether, except $\text{Ni}(\text{CO})_4$ which produced only methanol. However, it was still not clear whether the results for group 6 metal carbonyls are due to the typical methoxide carbonylation mechanism, Scheme 1 [11,24], or whether another mechanism involving an active intermediate, such as the metalloester (Eq. (2)), is dominating in this catalysis. The role of $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ in the formation of methanol under CO atmosphere is not yet understood, while the role of $\text{W}(\text{CO})_6$ was studied by Darensbourg et al. [7,17] and some similarities might be expected.

Since there has been no clear explanation of the role of $\text{Mo}(\text{CO})_6$ in the formation of methyl formate and dimethyl ether, a fundamental study to examine the separate catalytic effect of potassium

methoxide (KOCH_3), $\text{Mo}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6/\text{KOCH}_3$ under CO, H_2 and syngas (1:1) atmosphere was undertaken.

2. Experimental

2.1. Materials

$\text{Mo}(\text{CO})_6$ and methanolic KOCH_3 were purchased from Sigma–Aldrich, while CO, H_2 and syngas (1:1) were obtained from Afrox (HP or UHP grades) and used without any further purification. Methanol was dried by refluxing over magnesium iodide followed by distillation. Tetrahydrofuran (THF) was dried by refluxing over sodium benzophenone under nitrogen. Triglyme was dried over sodium wire and used without distillation. HP-IR spectra were recorded in a high pressure IR cell with CaF_2 windows at Sasol Technology R&D using a Bruker Equinox 55 instrument. GC and GC–MS analyses of the organic products were analyzed by Perkin Elmer Clarus 500 instruments. Reactions in THF and triglyme were identical to those described for methanol below, except that the relevant solvent replaced methanol.

2.2. Reactions

2.2.1. Catalytic reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 in methanol under CO atmosphere

$\text{Mo}(\text{CO})_6$ (2.64 g, 10 mmol) was added to dry MeOH (20 ml) and transferred to a pipe reactor. A methanolic solution of KOCH_3 (10 ml, 2.5 g, 35 mmol) was added. The reactor was purged three times with carbon monoxide, after that 1.60 MPa of CO was charged. The reactor was then heated while stirring in an oil bath at 160°C for 24 h.

2.2.2. Catalytic reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 in methanol under CO/H_2 atmosphere

The experimental procedure described in Section 2.2.1 was used, except that the reactor was charged with syngas (1:1).

2.2.3. Catalytic reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 in methanol under H_2 atmosphere

The experimental procedure described in Section 2.2.1 was used, except that the reactor was charged to 1.10 MPa with H_2 .

2.2.4. HP-IR studies of the reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 under CO, H_2 and syngas atmosphere

$\text{Mo}(\text{CO})_6$ (52 mg, 0.19 mmol) was dissolved in dry THF (20 ml) and transferred to a high pressure IR cell equipped with CaF_2 windows. A methanolic solution of KOCH_3 (0.3 ml, 66.4 mg, 0.95 mmol) was added to the reactor, which was then pressurized with 0.50 MPa of each gas or gas mixture and stirred while the reaction was monitored by IR as the cell was heated from room temperature to 100°C . The spectra were collected every 10 min during the reaction.

3. Results and discussions

3.1. Catalytic studies

The solvents (methanol, THF and triglyme) were selected based on their polarity. In all solvents $\text{Mo}(\text{CO})_6$ alone displayed no catalytic activity under CO, H_2 and syngas atmospheres. A considerable amount of methyl formate, formic acid and dimethyl ether was produced over KOCH_3 in all solvents under CO and syngas atmosphere. Dimethyl ether was associated with the dehydration of methanol [24], while formic acid was probably formed by the hydrolysis of methyl formate.

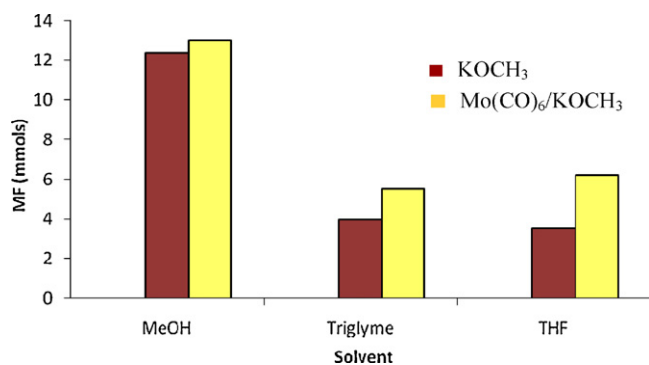


Fig. 1. The effect of Mo(CO)₆ and solvent in CO carbonylation of CH₃OH, 1.60 MPa CO at 125 °C.

3.1.1. Under CO pressure

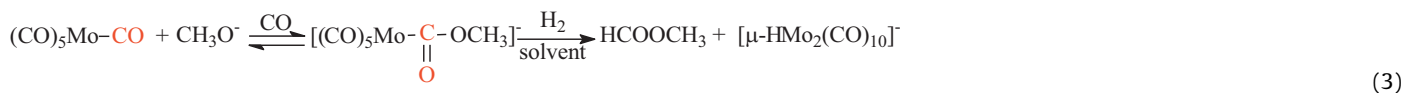
When the same reactions were performed over Mo(CO)₆:KOCH₃ (1:3) under carbon monoxide atmosphere, the amount of methyl formate produced increased very slightly compared to the KOCH₃ catalyst alone in all cases (Fig. 1). This is associated to the nucleophilic attack of KOCH₃ on the metal coordinated carbon monoxide (Eq. (2)), which is presumed to be faster than the competing attack of KOCH₃ on the free carbon monoxide (Eq. (1)) [7,20].

The amount of methyl formate produced was significantly higher in methanol compared to the other solvents due to the regeneration of the methoxide, while in THF and triglyme the methanol from the added KOCH₃ solution is consumed and thus the regeneration of the methoxide is inhibited, reducing the amount of methyl formate produced. The step involving the protonation of the metalloester by methanol to eliminate methyl formate is seen as the central step in these reactions (Eq. (2)), which also allows prediction of which system might produce more methyl formate. Darensbourg et al. [17] reported that the reaction of W(CO)₆ and methoxide anion in pure THF did not produce methyl formate, which implies that a small amount of methanol in the Mo(CO)₆/KOCH₃/THF/CO system might shift the reaction to a product, but only to a certain extent.

The results under CO atmosphere correlate with those reported for the W(CO)₆/KOCH₃ system [7,17], although the effect of Mo(CO)₆ is not seven times that of KOCH₃.

3.1.2. Under H₂ pressure

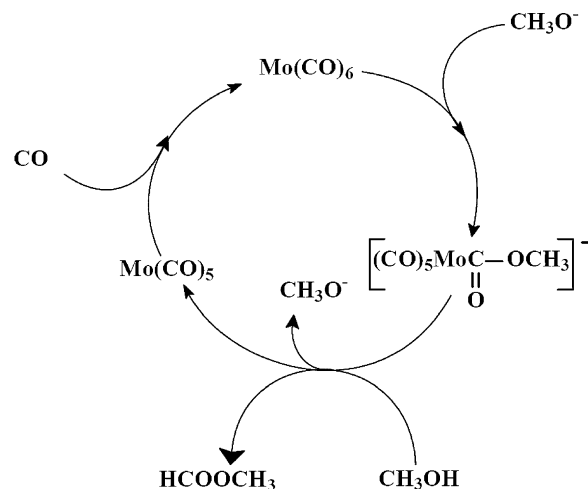
The reaction of Mo(CO)₆/KOCH₃ under H₂ atmosphere in the THF/MeOH mixture produced methyl formate in amounts comparable to those obtained in the reaction performed under CO atmosphere (Fig. 2). This suggests that under a hydrogen atmosphere, the metalloester (Eq. (3)) is hydrogenated in situ to form methyl formate. FTIR analysis of the organometallic product showed peaks corresponding to the formation of the metalloester (IR bands at 2030(w) cm⁻¹, 1940(s) cm⁻¹, 1878(m) cm⁻¹, 1610(s) cm⁻¹) and methyl formate (IR band at 1732 cm⁻¹).



3.1.3. Under syngas pressure

Comparing the reactions performed under CO and syngas atmosphere in methanol, the results show that more methyl formate is produced under syngas than CO atmosphere in both the KOCH₃ and Mo(CO)₆/KOCH₃ catalyzed experiments (Figs. 1 and 3).

The results of Mo(CO)₆/KOCH₃ under syngas atmosphere are not extraordinary based on the fact that the synthesis gas utilized was made up of equivalent amounts of CO and H₂ (1:1). Therefore some methyl formate will be generated through the H₂ mechanism,



Scheme 2. CO dominated mechanism for the formation of methyl formate from Mo(CO)₆/KOCH₃ under syngas atmosphere.

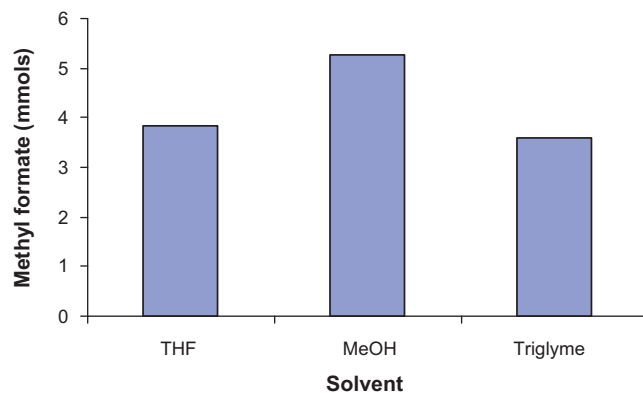


Fig. 2. Methyl formate from Mo(CO)₆/KOCH₃/H₂ in different solvents.

which involves hydrogenation of the metalloester (Eq. (3)). Another possibility might involve a CO mechanism (Scheme 2).

In support of Eq. (3), high pressure IR (HP-IR) analysis of the same reaction (*vide infra* Section 3.2.2) showed growing peaks characteristic of the stable bridged hydride ([μ-HMo₂(CO)₁₀]⁻) at 2041(w) cm⁻¹, 1944(vs) cm⁻¹, 1881(m) cm⁻¹ as the peaks characteristic of the metalloester ([Mo(CO)₅(COOCH₃)]⁻) at 2052(w) cm⁻¹, 1912(s) cm⁻¹, 1881(m) cm⁻¹, 1600(m, br) cm⁻¹ decreased (*note*: A peak at 1678 cm⁻¹ was associated with the formation of a *bis*(methoxycarbonyl) complex). The methyl formate peak was observed at 1734(m, br) cm⁻¹.

The CO mechanism involves the nucleophilic attack on the metal coordinated CO by CH₃O⁻ and protonation of the metalloester intermediate [(CO)₅Mo-COOCH₃]⁻ by methanol

under CO atmosphere to eliminate methyl formate as shown in Scheme 2. As described in Scheme 1, there exists a possibility that some methyl formate is generated from the methoxide carbonylation of methanol. The inhibition of methyl formate production in the presence of hydrogen is not significant in this case [7].

When comparing the reactions performed under CO and syngas atmosphere in THF and triglyme (Figs. 1 and 3), the amount of methyl formate produced in the reaction under syngas is less than that produced under CO atmosphere. This can be due

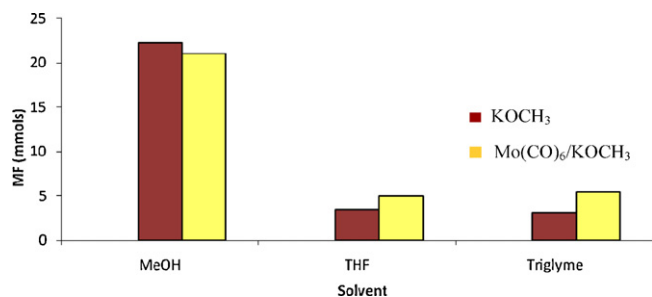


Fig. 3. Methyl formate from Mo(CO)₆/KOCH₃/syngas in different solvents.

to the formation of other organic products, which cannot form under CO atmosphere alone. Analysis of the organic products from the Mo(CO)₆/KOCH₃/syngas system in triglyme (Fig. 4) revealed the formation of longer chain alcohols (C2–C5), namely ethanol, 2-propanol, 2-butanol, 3-methyl-2-butanol, 3-pentanol, 2-methyl-3-pentanol and 2,4-dimethyl-3-pentanol in addition to methyl formate and dimethyl ether. There were no other organic products observed for the reactions performed under syngas atmosphere in the THF. The alcoholic products (Fig. 4) might be expected in a CO hydrogenation reaction catalyzed by a molybdenum catalyst, since supported Mo catalysts have been used for CO hydrogenation to produce higher (C1–C6) alcohols [25–28]. The stoichiometric effect of Mo(CO)₆ in the production of methyl formate was considered only in THF under syngas (1:1), by varying its amount relative to potassium methoxide. The results reported in Figs. 1–4 thus far were performed at a stoichiometric ratio of Mo(CO)₆:KOCH₃ of 1:4. The ratios of Mo(CO)₆:KOCH₃ studied were 1:4, 1:2, 1:1 and 2:1. The results show that the amount of methyl formate formed initially increases with the amount of Mo(CO)₆ added. However, a stoichiometric ratio of 1:2 gave the best results (Fig. 5). This shows that Mo(CO)₆ does not significantly react with water (in the WGSR) as there is no linear response to methyl formate as its amount increases.

3.2. In situ IR studies of the reaction of Mo(CO)₆ and KOCH₃ under different gases

3.2.1. In situ studies of the reaction of Mo(CO)₆ and KOCH₃ under CO pressure

Mo(CO)₆ rapidly reacts with KOCH₃ under CO pressure (0.50 MPa, 13 °C) to form [Mo(CO)₅(COOCH₃)]⁻, which is characterized by IR peaks at 2054(w) cm⁻¹, 1915(s) cm⁻¹, 1882(s) cm⁻¹ and 1610 (m, br) cm⁻¹, Fig. 6 [29]. The Mo(CO)₆ (peak at 1990 cm⁻¹) decreased immediately after mixing the reactants and was not

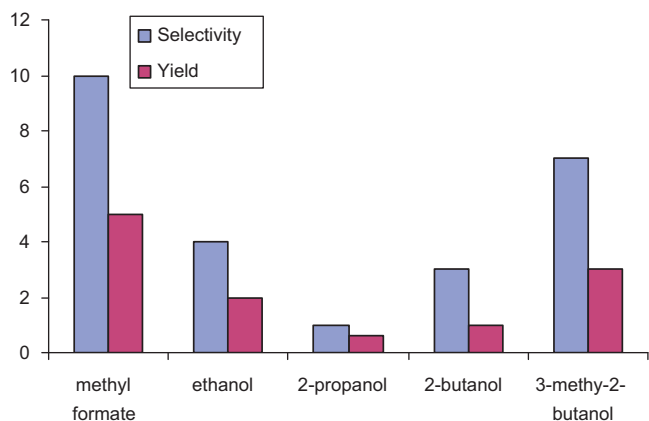


Fig. 4. Selectivity of higher alcohols in Mo(CO)₆/KOME/syngas (1:1) in triglyme.

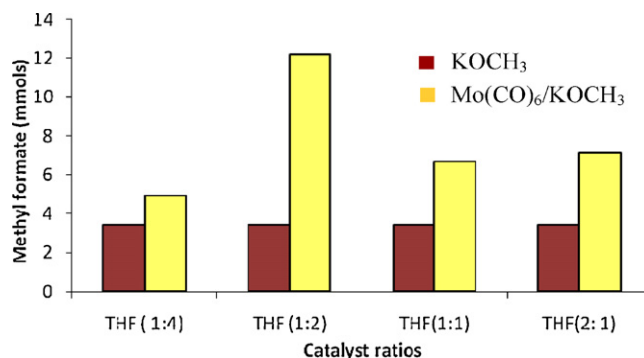


Fig. 5. Stoichiometric effect of Mo(CO)₆:KOCH₃ under syngas (1:1) atmosphere in THF.

subsequently observed at this temperature (13 °C). The peak at 1730 cm⁻¹, assigned to the carbonyl peak of methyl formate (formed probably due to the reaction between CO and CH₃O⁻) grew as the reaction progressed, while the peaks of [Mo(CO)₅(COOCH₃)]⁻ remained constant. Carbon monoxide stabilizes the [Mo(CO)₅(COOCH₃)]⁻ species, but as the temperature was increased from room temperature to 100 °C, the peaks for [Mo(CO)₅(COOCH₃)]⁻ at 2054 cm⁻¹, 1915 cm⁻¹, 1882 cm⁻¹ and 1610 cm⁻¹ decreased, while the Mo(CO)₆ peak at 1990 cm⁻¹ and the methyl formate peak at 1730 cm⁻¹ increased (indicated with the arrows in Fig. 6). At 100 °C all the peaks assigned to [Mo(CO)₅(COOCH₃)]⁻ in the carbonyl region (2100–1800 cm⁻¹) had decreased and a new species formed with peaks at 1927(m) cm⁻¹ and 1882(w) cm⁻¹. The methyl formate peak remained at 1730 cm⁻¹, while the peak at 1610 cm⁻¹ (Mo–COOMe) decreased and peaks at 1617(sh) cm⁻¹ and 1594 cm⁻¹ were observed (Fig. 6).

There was no evidence of the formation of [Mo₃(CO)₉(OCH₃)₃]⁻ during the reaction of Mo(CO)₆ and KOCH₃ [30,31]. An increase in the Mo(CO)₆ peak intensity suggests that the metalloester [Mo(CO)₅(COOCH₃)]⁻ is protonated by methanol to eliminate methyl formate and form the reactive Mo(CO)₅ and CH₃O⁻ species. Mo(CO)₅ then reacts with CO to regenerate Mo(CO)₆ (Scheme 2). There exist a possibility of a slow reaction between the Mo(CO)₅ intermediate and CH₃O⁻ to form [Mo(CO)₅(OCH₃)]⁻. The existence of [Mo(CO)₅(OCH₃)]⁻ was tentatively associated with the peaks at 1927(m) cm⁻¹ and 1882(w) cm⁻¹, 1617 cm⁻¹ and 1594 cm⁻¹, from Scheme 2 (vide supra) [Mo(CO)₅(OCH₃)]⁻, seemed to be the only

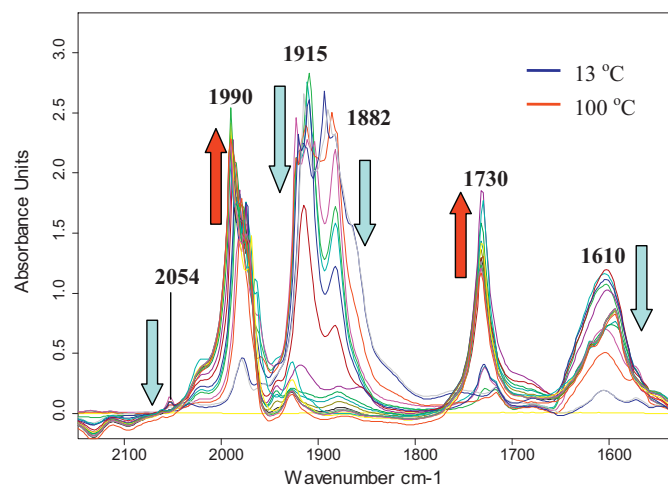


Fig. 6. HP-IR spectra for the reaction of Mo(CO)₆ with KOCH₃ (1:5) under CO pressure.

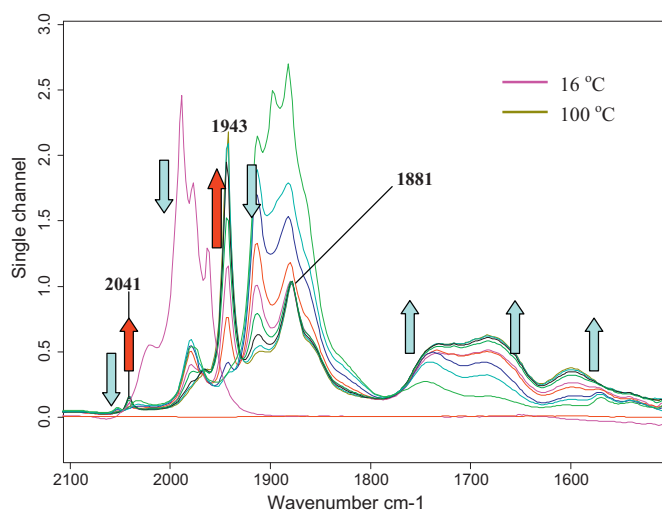
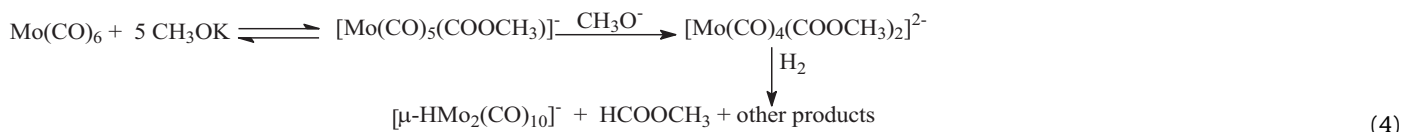


Fig. 7. HP-IR spectra for the reaction of $\text{Mo}(\text{CO})_6$ with KOCH_3 (1:5) under H_2 pressure.

final product that can be formed from the reaction of $\text{Mo}(\text{CO})_5$ and CH_3O^- .

3.2.2. In situ studies of the reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 under H_2 pressure

The reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 under H_2 pressure was performed to investigate the role of H_2 in the formation of methyl formate. The reaction was carried out under 0.50 MPa H_2 , from 16 °C to 100 °C. $\text{Mo}(\text{CO})_6$ rapidly reacted with KOCH_3 to produce $[\text{Mo}(\text{CO})_5(\text{COOCH}_3)]^-$, which was characterized by peaks at 2054(w) cm^{-1} , 1914(s) cm^{-1} , 1881(m) cm^{-1} and 1570(vw) cm^{-1} (Fig. 7). As the reaction proceeded, the peaks at 1732(sh) cm^{-1} and 1680(sh) cm^{-1} grew. The peak at 1732 cm^{-1} could be assigned to the carbonyl peak of methyl formate and the peak at 1680 cm^{-1} was assigned to the metal coordinated methyl ester ($\text{Mo}-\text{COOCH}_3$) group. The peaks characteristic of molybdenum pentacarbonyl (2054 cm^{-1} , 1914 cm^{-1} and 1881 cm^{-1}) decreased as the peaks for the methyl formate and ester ($\text{Mo}-\text{COOCH}_3$) grew. After a further 10 min a peak at 1600 cm^{-1} began to grow in conjunction with the peaks at 1732 and 1680 cm^{-1} (Fig. 7). This could indicate the possible formation of a bis(methoxycarbonyl) complex due to excess KOCH_3 in the system (Eq. (4)) [32].



The peaks at 2054 cm^{-1} , 1914 cm^{-1} and 1881 cm^{-1} decreased very rapidly as the reaction proceeded to generate a new Mo carbonyl species with peaks at 2041(w) cm^{-1} , 1943 (vs) cm^{-1} , 1881(m) cm^{-1} (Fig. 7), which were assigned to $[\mu\text{-HMo}_2(\text{CO})_{10}]^-$. The peak due to the mono hydride species ($[\text{HMo}(\text{CO})_5]^-$) was observed as a shoulder (1860 cm^{-1}) in Fig. 7 but in Fig. 8 the individual peak for this species can be observed [33]. It is important to note that the $\text{Mo}(\text{CO})_6$ peak at 1978 cm^{-1} started disappearing as the peaks for $[\mu\text{-HMo}_2(\text{CO})_{10}]^-$ species started growing. The reaction is summarized in Eq. (4). The stable bridged hydride $[\mu\text{-HMo}_2(\text{CO})_{10}]^-$ could form through the reaction of the unstable $[\text{HMo}(\text{CO})_5]^-$ with $\text{Mo}(\text{CO})_6$ (Eq. (5)) [33–36].

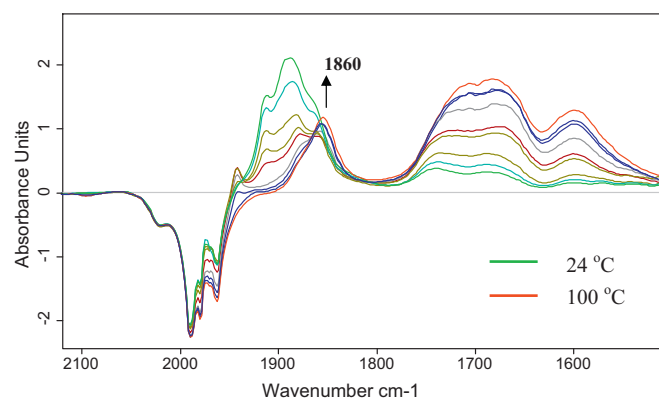


Fig. 8. HP-IR spectra showing peak representing a mono hydride ($[\text{HMo}(\text{CO})_5]^-$).

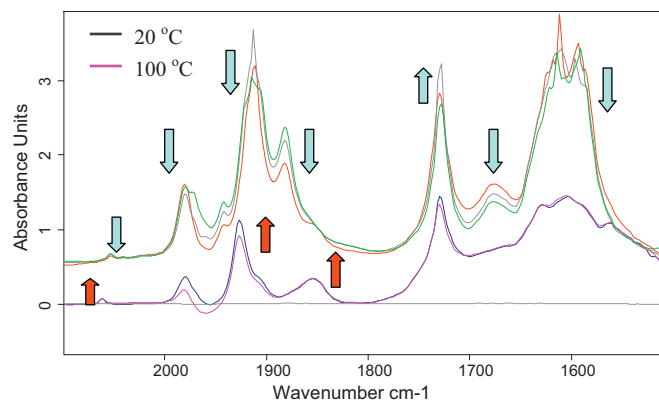


Fig. 9. HP-IR spectra for the reaction of $\text{Mo}(\text{CO})_6$ with KOCH_3 (1:5) under syngas pressure.

The concentration of $[\text{Mo}(\text{CO})_5(\text{COOCH}_3)]^-$, with peaks at 2054 cm^{-1} , 1914 cm^{-1} and 1881 cm^{-1} , decreased under H_2 pressure until it reached an equilibrium state with the bridged hydride $[\mu\text{-HMo}_2(\text{CO})_{10}]^-$ which also has a peak at 1881 cm^{-1} . Upon heating, the bridged hydride is further converted to a ($[\text{HMo}(\text{CO})_5]^-$) species which shows a single peak at 1860 cm^{-1} (Fig. 8).

3.2.3. In situ studies of the reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 under syngas (1:1) pressure

The formation of methyl formate from the reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 was carried out under syngas (1:1) pressure to investigate which species would be formed predominantly and determine whether it formed as a result of the CO or H_2 . The first carbonyl species observed was $[\text{Mo}(\text{CO})_5(\text{COOCH}_3)]^-$, characterized by peaks at 2053(w) cm^{-1} , 1914(s) cm^{-1} , 1881(m) cm^{-1} and 1600(m, br) cm^{-1} (Fig. 9). As the reaction progressed, the carbonyl peak for methyl formate at 1729(s) cm^{-1} began to grow, as did peaks at 2041(vw) cm^{-1} and 1943(sh) cm^{-1} characteristic of the bridged hydride species (the peak at 1881 cm^{-1} overlaps with that

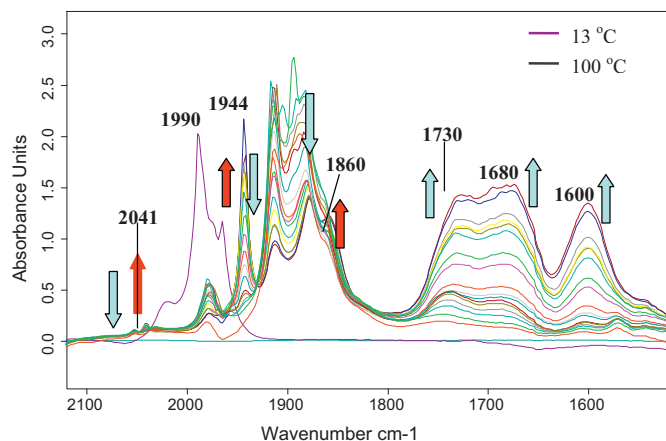
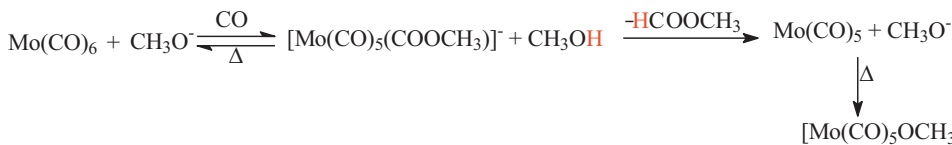


Fig. 10. HP-IR spectra for the reaction of $\text{Mo}(\text{CO})_6$ with KOCH_3 (1:5) under N_2 pressure.

of the metalloester). A peak at 1675 cm^{-1} was also observed as the reaction progressed.

As heating began, the peaks characteristic of $[\text{Mo}(\text{CO})_5(\text{COOCH}_3)]^-$ (2054 cm^{-1} , 1914 cm^{-1} , 1881 cm^{-1} and 1600 cm^{-1}) decreased while new species $[\text{Mo}(\text{CO})_5\text{OCH}_3]^-$, with peaks at $2060(\text{w})\text{ cm}^{-1}$, $1925(\text{s})\text{ cm}^{-1}$, $1852(\text{m})\text{ cm}^{-1}$, $1620(\text{sh})\text{ cm}^{-1}$ and $1593(\text{m})\text{ cm}^{-1}$ grew (Eq. (6)). The species $[\text{Mo}(\text{CO})_5\text{OCH}_3]^-$ is probably formed through a competing reaction of the $\text{Mo}(\text{CO})_5$ intermediate (Scheme 2) with CH_3O^- and CO, in which case the reaction shown in Eq. (6) is the major reaction under syngas atmosphere. This dominance might be associated with the presence of hydrogen which might weakly block the vacant site of $\text{Mo}(\text{CO})_5$ through the possible formation of the $\text{Mo}(\text{CO})_5(\text{H}_2)$ species which was, however, not observed [37].



The $[\text{Mo}(\text{CO})_5\text{OCH}_3]^-$ species has not been previously characterized, but based on the comparison of the peak shifts of $[\text{PPN}][\text{W}(\text{CO})_5\text{O}_2\text{CCF}_3]$ and $[\text{PPN}][\text{Mo}(\text{CO})_5\text{O}_2\text{CCF}_3]$, the species was assigned as $[\text{Mo}(\text{CO})_5\text{OCH}_3]^-$. The peak difference for the E band between $[\text{PPN}][\text{W}(\text{CO})_5\text{O}_2\text{CCF}_3]$ and $[\text{PPN}][\text{Mo}(\text{CO})_5\text{O}_2\text{CCF}_3]$ is 23 cm^{-1} [38–40]. The difference between the E band of $[\text{W}(\text{CO})_5\text{OCH}_3]^-$ and the postulated $[\text{Mo}(\text{CO})_5\text{OCH}_3]^-$ is 24 cm^{-1} . The final species under syngas pressure is the same as for the species observed for the reaction under CO pressure, which implies that the dominating mechanism under syngas is the CO

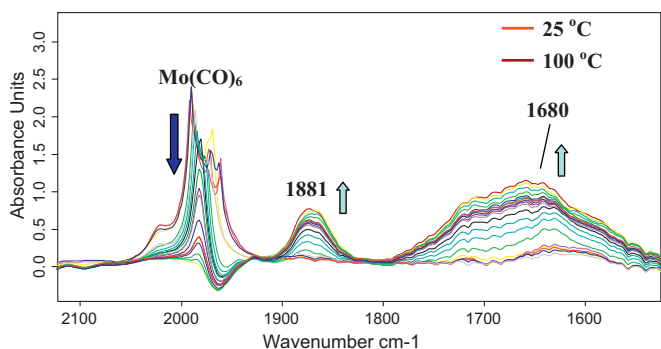


Fig. 11. HP-IR spectra for the reaction of $\text{Mo}(\text{CO})_6$ with CH_3ONa (1:5) under N_2 pressure in only THF.

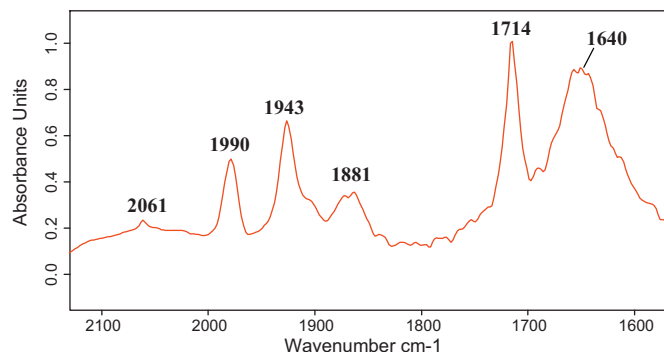


Fig. 12. HP-IR spectra for the reaction of $\text{Mo}(\text{CO})_6$ with CH_3ONa (1:5) under N_2 pressure in THF after addition of MeOH.

mechanism. The peaks at 2041 cm^{-1} , 1943 cm^{-1} and 1675 cm^{-1} also disappeared towards the end of the reaction (Fig. 9).

3.2.4. In situ studies of the reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 under N_2 pressure

The reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 was studied under N_2 to investigate the effect of methanol in the formation of methyl formate. As in previous experiments, $\text{Mo}(\text{CO})_6$ rapidly reacted with KOCH_3 methanolic solution under N_2 to form the metalloester $[\text{Mo}(\text{CO})_5(\text{COOCH}_3)]^-$ (peaks at $2054(\text{vw})\text{ cm}^{-1}$, $1915(\text{s})\text{ cm}^{-1}$, $1881(\text{s})\text{ cm}^{-1}$ and a shoulder at 1680 cm^{-1}) (Fig. 10). As the reaction progressed, a peak at 1730 cm^{-1} associated to the carbonyl peak of methyl formate grew together with new peaks at 1680 and 1600 cm^{-1} , characteristic of a bis(methoxycarbonyl) complex. At $80\text{ }^\circ\text{C}$, the bridged hydride characterized by peaks at $2041(\text{w})\text{ cm}^{-1}$, $1943(\text{vs})\text{ cm}^{-1}$ and an overlapping peak at $1881(\text{m})\text{ cm}^{-1}$ grew,

with the decrease in the metalloester species (with peaks at 2054 cm^{-1} , 1915 cm^{-1} and 1881 cm^{-1}).

Similar to the experiment under H_2 pressure, the peak at 1881 cm^{-1} assigned to the bridged hydride ($[\mu\text{-HMo}_2(\text{CO})_{10}]^-$) did not change further. This suggests that protonation of the metalloester $[\text{Mo}(\text{CO})_5(\text{COOCH}_3)]^-$ does occur without hydrogen being present, and the effect of the temperature shows that the system eliminates methyl formate at a lower temperature than $80\text{ }^\circ\text{C}$. This is in contrast to the $\text{W}(\text{CO})_6/\text{KOCH}_3$ system, where Darensbourg et al. [17] found that methyl formate was eliminated at $100\text{ }^\circ\text{C}$.

On addition of MeOH, the peaks assigned to the bridged hydride ($[\mu\text{-HMo}_2(\text{CO})_{10}]^-$) also decreased during the heating process to form a mono hydride compound with a peak at 1860 cm^{-1} . It is important to note that this transformation is not possible without the addition of methanol to the reaction $\text{Mo}(\text{CO})_6/\text{CH}_3\text{ONa}/\text{N}_2$ (Fig. 11), however, upon addition of 1.25 ml of MeOH to the reaction $\text{Mo}(\text{CO})_6/\text{CH}_3\text{ONa}/\text{N}_2$ a new compound with peaks at $2061(\text{w})\text{ cm}^{-1}$, $1943(\text{s})\text{ cm}^{-1}$, $1714(\text{s})\text{ cm}^{-1}$ and $1640(\text{s, br})\text{ cm}^{-1}$ is also formed (Fig. 12).

4. Conclusions

The addition of $\text{Mo}(\text{CO})_6$ to the methoxide carbonylation of methanol under CO atmosphere increases the amount of methyl formate produced. The effect of solvent is very important in this reaction. Excess methanol increases the formation of methoxide

ion, while reaction in THF and triglyme produce lower amounts of methyl formate. This is probably due to the inability of THF and triglyme to protonate the metalloester $[(\text{CO})_5\text{Mo}(\text{COOCH}_3)]^-$. The same solvent effect was observed under H_2 and syngas atmosphere.

Addition of $\text{Mo}(\text{CO})_6$ to the methoxide carbonylation of methanol under syngas produced more methyl formate in methanol solution than in THF and triglyme. This is probably due to the hydrogen in syngas, which assists in the hydrogenation of the metalloester. A stoichiometric increase in the $\text{Mo}(\text{CO})_6$ ratio under syngas (1:1) increased the amount of methyl formate produced, with a 1:2 ratio of $\text{Mo}(\text{CO})_6$: KOCH_3 producing more methyl formate compared to the other ratios. This shows that $\text{Mo}(\text{CO})_6$ does not significantly react with water in the water gas shift reaction as there is no linear response of methyl formate to the increase in $\text{Mo}(\text{CO})_6$ concentration. Long chain (C2–C5) alcohols were also produced in triglyme. The reaction of $\text{Mo}(\text{CO})_6$ and KOCH_3 under H_2 produced comparable amounts of methyl formate as the reaction performed under CO atmosphere.

HP-IR studies of $\text{Mo}(\text{CO})_6$ and KOCH_3 (1:5) performed under CO atmosphere produced the metalloester, which diminishes on elimination of methyl formate and regenerates $\text{Mo}(\text{CO})_6$. If the same reaction is performed under H_2 atmosphere, the metalloester is formed, which then diminishes on forming the bridged hydride $[\mu\text{-HMo}_2(\text{CO})_{10}]^-$. Addition of excess CH_3O^- under H_2 atmosphere results in the formation of a bis(methoxycarbonyl) complex. A peak characteristic of a mono hydride was only observed at higher temperatures (100 °C).

HP-IR studies of $\text{Mo}(\text{CO})_6$: KOCH_3 (1:5) under syngas showed the formation of the bridged hydride $[\mu\text{-HMo}_2(\text{CO})_{10}]^-$ which disappeared after a few minutes of the reaction on forming the methoxide complex $(\text{Mo}(\text{CO})_5\text{OCH}_3)^-$ as the end point of the reaction. A bis(methoxycarbonyl) complex is not observed under CO atmosphere, which implies that some excess CH_3O^- catalyzes the carbonylation reaction to form methyl formate. $\text{Mo}(\text{CO})_6$ therefore increased the formation of methyl formate from the carbonylation of methanol, as it provided a more electrophilic coordinated CO as compared to the free carbon monoxide.

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