The Role of Iodide Promoters and the Mechanism of Ethylene Carbonylation Catalyzed by Molybdenum Hexacarbonyl

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Abstract: In limited prior reports, molybdenum hexacarbonyl has been shown to be active in catalyzing ethylene carbonylation promoted by ethyl iodide. Here, we assess the productivity of this reaction with respect to various reaction parameters and provide an understanding of the mechanism by NMR and mass spectrometric studies of isotopically-labeled reactants. ¹³C labeled reactants show that ethyl iodide promotes initiation but is not a participant in the primary catalytic cycle, in contrast to classical mechanisms for alcohol carbonylation with an iodide co-catalyst, such as in the Monsanto process. NMR spectroscopy shows incorporation of only one D from D₂O into the carbon backbone of propionic acid products, and in a manner consistent with direct, reversible addition of ethylene to a Mo-hydride intermediate. CO migratory insertion and a formal hydroxylation then yield propionic acid. Under the conditions described here, the overall cycle gives propionic acid in high selectivity and requiring low promoter loads.

Keywords: homogeneous catalysis, carbonylation, ethylene, isotopic labeling, promotion, molybdenum, metal carbonyl

1. Introduction

Alkene carbonylation is an important route to alkanolic acid intermediates which can be used as chemical feedstocks.[1] Carbonylation of alkenes, alkynes, and alcohols catalyzed by metal carbonyls was first developed by W. Reppe et al. at BASF in the 1930s and 1940s.[2] Ethylene carbonylation can produce propionic acid (PA) using a Ni(CO)_4 catalyst at 100-300 bar and 250-320°C.[3-6] Iodide-promoted group VI metal hexacarbonyls (Cr, Mo, or W) have been reported to be active for the carbonylation of ethylene to propionic anhydride or propionic acid when water is added to the reactants. [7, 8] They are less toxic and can operate under milder conditions (25-70 bar and 150-200°C) than the analogous Ni carbonyls.[3, 9, 10] Mo(CO)_6 has been reported to give the highest productivity (71 mol of propionic anhydride per mole of Mo(CO)_6 per hour) among the group VI hexacarbonyls.[7, 11] However, the group VI catalysts require iodide promoters that are corrosive and thus can lead to increased production costs. Understanding the mechanism for carbonylation with Group VI metal carbonyls could potentially lead to process enhancements.

Methanol carbonylation catalyzed by Rh or Ir carbonyl catalysts, e.g. the Monsanto process, is well studied. In that process, methyl iodide is generated by the reaction of methanol with hydroiodic acid. Oxidative addition of methyl iodide is followed by migratory insertion of a CO ligand, and the reductive elimination of acetyl iodide.[12-14] Water reacts with this acetyl iodide to form acetic acid and hydroiodic acid, generating product and restarting the cycle.[15, 16] The iodide is thus a co-catalyst required for each catalytic turnover.

Analogous mechanistic detail is limited for alkene carbonylation with Group VI metal carbonyls. In one of the few prior detailed studies, Zoeller and co-workers investigated Mo-catalyzed ethylene carbonylation to yield propionic anhydride.[7] They proposed a free-radical process initiated by the rate-limiting dissociation of CO from Mo(CO)_6 . Ethyl iodide (EtI) reacts with coordinatively unsaturated Mo(CO)_5 to form a $\text{Mo(CO)}_5\text{I}^\bullet$ radical and ethyl radicals (1.1).

These ethyl radicals are then proposed to react with Mo(CO)_6 to form the pivotal complex, $[\bullet\text{Mo(EtCO)(CO)}_5]$.

The $\text{Mo(CO)}_5(\text{EtCO})\bullet$ complex allows entry into a catalytic radical chain that adds ethylene to a Mo hydride and eventually forms propionyl iodide. In their study, propionyl iodide is proposed to subsequently react with propionic acid to form propionic anhydride. In follow up studies, Zoeller et. al. observed Mo(CO)_6 and a number of adducts of unsaturated Mo carbonyls using *in-situ* infrared spectroscopy.[11]

An intermediate approach to ethylene carbonylation was examined by Roe et. al. [17] They studied the mechanism of Rh-catalyzed HI-promoted carbonylation of ethylene into propionic acid in a non-protic solvent. Starting from $[\text{Rh}(^{13}\text{CO})_2\text{I}_2]^-$, HI, and ethylene, $[(\text{CH}_3\text{-CH}_2^{13}\text{CO})\text{Rh}(^{13}\text{CO})\text{I}_2]^-$ was detected by ^{13}C -NMR spectroscopy. This species is consistent with oxidative addition of HI to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, forming a Rh hydride intermediate. Ethylene adds to the hydride, generating a Rh-alkyl and eventually propionic acid.

The current investigation uses labeled reactants ($\text{H}_3\text{C-}^{13}\text{CH}_2\text{I}$, $\text{H}_3\text{C-CD}_2\text{I}$, $\text{H}_2^{13}\text{C=}^{13}\text{CH}_2$, and D_2O) with GC-MS and ^{13}C NMR analysis of products to better understand the catalytic mechanism, with an emphasis on the steps required for insertion of an ethyl fragment into the catalytic cycle. The dependence of propionic acid yield and selectivity on promoter amount and identity, and the partial pressures of ethylene, CO, and H_2 are also discussed. The data suggest that the primary role of iodide is as a promoter that activates the Mo catalyst, and that ethylene adds directly to a proposed Mo hydride intermediate, giving a Mo ethyl and eventually propanoates. This leads to a simplified catalytic cycle for carbonylation with Mo(CO)_6 more akin to that proposed by Roe et. al. for $\text{Rh(CO)}_2\text{I}_2^-$ than the radical chain proposed by Zoeller et. al. for Mo(CO)_6 .

2. Experimental

2.1. Catalytic evaluation

All chemicals were obtained from Sigma-Aldrich and used without further purification. Following the conditions of the prior studies by Zoeller et al.[7, 11], the standard reaction mixture was prepared at room temperature and was composed of 1 mmol of Mo(CO)_6 , 1.3 mmol of tetrabutyl phosphonium iodide (TBPI), 76 mmol of ethyl iodide (EtI), 460 mmol of water and 760 mmol of acetic acid. Acetic acid solvent was

chosen for its stability under reaction conditions,[18] and to mimic the use of a propionic acid recycle while allowing easier quantification of reaction products; the acetate groups are not incorporated into any propanoate products. A 300 mL Hastelloy® C reactor was used for ethylene carbonylation experiments. This autoclave filled with the reaction mixture, and was pressurized with 10 bar N₂, vented, and repeated 4 times to remove gaseous and dissolved O₂. Then the reactor was charged with the reactant gas mixture. Approximately 1-2 mmol of EtI was lost during this venting/purging process. 10 ± 1 bar H₂, (99.999%), 10 ± 1 bar ethylene (99.999%), and 10 ± 1 bar CO (99.9995%) were sequentially admitted into the reactor at room temperature to reach a total pressure of 30 ± 1 bar. These pressures correspond to 91 ± 8 mmol of CO, C₂H₄ or H₂ being charged in the headspace of the reactor. Based on Henry's law constants for H₂O,[19] 0.7 mmol of CO, 3.5 mmol of C₂H₄ and 0.6 mmol of H₂ would be expected to dissolve at room temperature and 10 bar added pressure. Though the Henry's law constants for acetic acid are not readily available, slightly higher solubilities of each component are expected in the acetic acid solvent.[20] One consequence of these solubilities is that ethylene will always be in slight excess even if equal pressures are charged to the headspace. Over 0.6-1 hour, the sample temperature and pressure were equilibrated at 190°C and 46-47 bar. Reaction time t=0 was counted when the reaction temperature reached 190°C. A stirring rate of 900 rpm was used following experiments showing no increases in yield above that stir rate. Over the course of the reaction, the pressure decreased to 29-30 bar at temperature, and 12-14 bar when cool, primarily reflecting consumption of CO and ethylene. After 1-5 h at 190°C, the reactor was cooled to room temperature and a liquid sample aliquot was passed through a 0.1 µm PTFE filter for GC analysis using an Agilent 7890A GC-FID with a HP-INNOWAX column (50 m x 0.2 mm x 0.4 µm) in the CleanCat core facility. Propanoate yield was calculated relative to added CO, including CO present in Mo(CO)₆, unless otherwise stated. Propionic acid (PA), ethyl propionate (EP), propionaldehyde, ethyl acetate, diethyl ether (DEE) and ethanol were calibrated against known standards. The latter three are condensation products between EtI and solvent water or acetic acid. The headspace of most experiments was sampled after cooling to room temperature. No additional volatile products, such as ethane, acetaldehyde, or dimethyl ether, were detected. Procedures

required to decrease the gas pressures for sampling did not allow for quantification of gas phase components.

2.2. Isotopic labeling experiments

In some experiments D₂O, 99 atom% ¹³C-ethylene (¹³CH₂=¹³CH₂), 1-¹³C-ethyl iodide (CH₃-¹³CH₂-I), and 1,1-*d*₂-ethyl iodide (CH₃-CD₂-I) were used to replace water, ethylene and ethyl iodide, respectively. An Agilent 7975C GC-MS-FID and a VF-WAX column (30 m x 0.25 mm x 0.5 μm) in the CleanCat core facility were used in the identification and analysis of the extent of labeling of reaction products.

Liquid phase ¹³C nuclear magnetic resonance (NMR) and DEPT-135 (Distortionless Enhancement by Polarization Transfer) spectra were recorded with a Bruker Avance-III spectrometer (125 MHz for ¹³C) equipped with a DCH cryoprobe. After 2 h of reaction at 190 °C, a sample of propionic acid was extracted from the reaction mixture by filtering off 20 mL of the reaction solution and extracting with 200 mL cold deionized water to remove residual Mo(CO)₆ and EtI as a separate phase. The aqueous phase was extracted with 200 cm³ hexanes to remove water-miscible TBPI. The organic phase was concentrated by rotary evaporation and dissolved into DMSO-*d*₆ for ¹³C-NMR and DEPT-135 experiments. The resulting sample contained PA with trace amounts of EP, ethyl acetate, and acetic acid.

3. Results and Discussions

3.1. The effect of the partial pressure of gas reactants on ethylene carbonylation

Table 1 shows the effect of the reactant pressure on the product distribution. Propionic acid (PA) is the major product, with lesser amounts of ethyl propionate (EP) and the condensation co-products ethyl acetate, ethanol, and DEE. The latter are not formed in the absence of added EtI (e.g. Table 2, entries 1 and 2). Yields are generally given for the sum of both propanoates, to indicate total carbonylation activity. In most experiments, dark precipitates may be isolated by filtration after reaction. X-ray diffraction of these precipitates is most consistent with graphitic coke (see Supporting Information Figure S1), but the presence of insoluble Mo species cannot be ruled out completely. In the absence of Mo(CO)₆, neither propionates nor coke were formed.

In absence of added CO, PA is still observed, corresponding to incorporation of approximately half of the CO in the added Mo(CO)_6 , and suggesting that a molybdenum tricarbonyl is a stable species under reaction conditions. 5-h molar yields of PA increased in proportion to the CO partial pressure, and condensation products remained low. In the absence of added ethylene, EtI provided ethyl groups for limited PA production. At 5 bar added ethylene, PA yields exceeded that of the added ethylene, indicating incorporation of EtI into products, but conversion was incomplete. Increasing ethylene pressure to 10 or 16 bar gave near 100% propanoate yields based on added CO. Condensation products such as EP also increased monotonically with ethylene pressure, suggesting the formation of additional EtI at high ethylene partial pressure. Propanoate yields suffered in the absence of H_2 , but were 90-100% as the H_2 partial pressure increased from 6 to 16 bar, indicating that H_2 plays a role in stabilizing the reaction, but not directly in the catalytic cycle, as expected. The 12-14 bar pressure remaining after typical reaction conditions is consistent with low consumption of H_2 . At high H_2 partial pressure, <0.5 mmol propionaldehyde (a hydroformylation product) was also detected; no further reduction products such as *n*-propanol were detected. Overall, standard conditions (1 mmol Mo(CO)_6 , 1.3 mmol Bu_4PI , 76 mmol EtI, 460 mmol H_2O , 760 mmol acetic acid, and 10 bar each H_2 , C_2H_4 and CO) gave $>90\%$ propanoate yields after 5 h at 190°C . It is not known at this time if the reduced yields at lower partial pressures of CO or ethylene are limited by rate or catalyst deactivation. Added H_2 appears to play several roles. First, we observe less formation of the insoluble precipitates at higher H_2 partial pressures, potentially improving catalyst lifetime and ethylene utilization. Added H_2 may also minimize CO loss from water-gas shift. Finally, Zoeller et al. observed a spectator Mo(II) species, $\text{Mo(CO)}_4\text{I}_3^-$, which was proposed to be re-reduced to catalytically active Mo(CO)_6 with added H_2 . [11]

3.2. Effect of iodides on propionic acid production

Table 2 shows the effect of EtI and TBPI on ethylene carbonylation product distributions. In the absence of any added iodide, 5h propanoate yield was $\sim 50\%$, indicating successful initiation of the catalytic cycle, perhaps directly through Mo hydrides formed from oxidative addition of H_2 or Mo ethyls formed from oxidative

addition of ethers or esters. The initial steps of such mechanisms would be analogous to those in the Heck-Breslow mechanism for alkene hydroformylation catalyzed by transition metal carbonyls.[21, 22] Consistent with prior reports,[7] adding only TBPI showed little improvement in yields. Addition of EtI only (entry 3) increased yields, but the PA yield remained lower than the amount of added EtI, making it uncertain whether ethylene was incorporated into the product. Given the small amounts of iodide from TBPI, we suggest that the counteranion may play a role in stabilizing partial negative charges on the catalyst. Zoeller et. al. suggested that partial decomposition of TBPI to a phosphine ligand may help stabilize the catalyst.[7] In either case, the role of the cation incorporated in the salt component is incompletely understood and requires separate investigation.

Entries 4-10 show that propanoate yields are ~100% at 5 h for between 3 and 76 mmol added EtI at a fixed 1.3 mmol TBPI. At lower levels, it is not known if rates or deactivation limit yields, but PA yields that exceed the added EtI do indicate that ethylene is being utilized successfully. At the highest levels of EtI, yields suffered slightly, suggesting a deactivation or inhibition route from excess iodide. Condensation products of EtI (e.g. ethyl propionate) increased with increasing added EtI, as expected.

Fig. 1(a) shows reactor composition vs. time at standard conditions. A 70% yield was reached in the first hour, then slowly rose to 99% over the next 5 hours. Within the precision of the results, the rate of PA production is near first order overall in the gaseous reactants (See Supporting Information Fig. S2). The turnover numbers measured are similar to those reported in the literature for comparable conditions.[7] During the first 5 h of reaction, a turnover number of 100 mol propionic acid/mol Mo was obtained. EtI decreases significantly during the first hour of reaction due to rapid reaction with solvent to form ethyl acetate and HI and, presumably, to initiation of the catalyst. The slow recovery of EtI in hours 1-5 is approximately first order in iodide, suggesting the slow re-equilibration between EtI, HI, and the small excess of ethylene that remains after complete CO consumption.[11] The net effect is to have little net EtI consumption after 5 h reaction. The fate of EtI will be discussed in later sections. Fig. 1(b) shows that after PA production has leveled off, PA production can be restored by recharging the gas phase reactants. After 3 h of reaction, the reactor was allowed to cool to room

temperature, de-pressurized, and recharged with 10 bar of H₂, 10 bar of C₂H₄ and 10 bar of CO. It was then heated to 190°C for another cycle of reaction without adding any additional ethyl iodide. After recharging the reactants and allowing the reaction to proceed for an additional 2 h, PA production (82 mmol PA in 2 h) was similar to the initial 2 h (84 mmol PA in 2 h). These data demonstrate that the leveling-off in propionic acid production after 3 h of reaction is due to the consumption of the reactants and that any inhibition that occurs in the first cycle is reversible.

Table 3 shows the results with different iodide promoters replacing EtI. Methyl iodide promoter gives PA yields only moderately lower than for EtI. 95% of the added MeI is consumed with relatively little formation of methyl acetate, indicating that the catalyst is readily initiated and (unobservable) acetic acid is formed. EtI and ethyl acetate are also formed, but at much lower levels than in the base case. A control reaction (Supporting Information Table S1) of MeI in propionic acid confirms that the majority of the MeI is carbonylated to acetic acid. With NaI, PA production was significantly lower than for either of the alkyl iodides. The production of EtI and ethyl acetate after 5 h was only approximately half of that for the MeI promoter. Inorganic iodide in the acetic acid solvent does not appear to be as effective a promoter, indicating that direct initiation by H⁺I may not compete with initiation by alkyl iodide. Likewise, EtI formation may also be catalyzed by an activated Mo species.

3.3. *Proposed reaction mechanism*

Fig. 2 illustrates the proposed reaction mechanism for iodide-promoted ethylene carbonylation with Mo(CO)₆. The reaction numbers refer to each step of the proposed mechanism. Reaction (1) is decarbonylation of the original hexacarbonyl. In reaction (2), EtI adds to the coordinately-unsaturated Mo complex **A** to give a Mo-iodide-ethyl complex **B**. An analogous initiation could take place readily with methyl iodide. This is followed by CO migratory insertion and re-carbonylation in reaction 3 to form **C**. Propionic acid is formed by the formal hydrolysis of **C**, reaction (4), giving Mo-hydride **D**. We will provide evidence that complex **C** does not proceed directly to **A** via loss of propanoyl iodide in step (5). Instead, we will show that complex **D** can directly add ethylene to recover the Mo-ethyl complex **B**, reaction (6). Step (7) accounts for

interconversion of **D** to **A** by loss of HI. This step also introduces the possibility of direct initiation to form **D** by addition of HI or some other species to **A**. Although iodide promoters were the focus of this investigation, we cannot rule out at this time direct roles for H₂O, H₂ or the solvent acetic acid itself. Thus, Fig. 2, uses **X** to denote one of the anionic ligands for the Mo complex, which may, in principle, be iodide, acetate, hydroxide, or hydride. Using these steps, the Mo catalyst is positioned to turn over the primary ethylene carbonylation cycle in one of two ways. A combination of steps (3), (4), and (6) turns over the catalyst without the use of alkyl iodide in the primary cycle. Alternately, steps (2), (3), (5) or (2), (3), (4), (7) turn over the catalyst with addition of the alkyl iodide co-catalyst required in every catalytic cycle. Distinguishing these two routes is the key question addressed in the following sections.

Reversible reactions external to the catalytic cycle include (8) ethylene addition to HI regenerating EtI and (9) condensation of EtI and PA leading to EP. Not shown are additional condensation reactions to form ethanol and DEE formation from EtI and water and ethyl acetate from acetic acid solvent, which are substantial sinks for alkyl iodides. HI is a co-product in reaction (9) and the condensation reactions.

3.4. Does propionic acid originate from ethyl iodide or ethylene?

It has been proposed earlier that ethyl iodide can initiate ethylene carbonylation catalyzed by Mo(CO)₆ to obtain a Mo-ethyl complex, but the nature of that initiation could only be inferred.[7, 11] As discussed in Section 3.3, ethyl fragments could be incorporated into product from EtI or directly from ethylene. EtI includes the originally added alkyl iodide, or as shown in Fig. 1(a), EtI regenerated from ethylene during reaction. To clarify which pathways contribute to products, we investigated the incorporation of isotopic labels in ethylene and ethyl iodide into propionic acid after 2 h of reaction. These conditions give approximately 90% propanoate yield and 40% EtI recovery as shown in Fig. 1(a).

Fig. 3 compares the GC-MS fragmentation patterns for PA obtained during reaction with 1-¹³C-ethyl iodide (H₃C-¹³CH₂I), 1,1-*d*₂-ethyl iodide (H₃C-CD₂I), or ¹³C ethylene (¹³CH₂=¹³CH₂) replacing the standard reactants. The MS spectra are normalized by the moles of propionic acid. Mass numbers (*m/z*) 73-76 contain incorporated ethyl groups;

patterns for the lighter fragments are given in Supporting Information Fig. S3. The fragmentation patterns obtained using labeled ethyl iodide ($\text{H}_3\text{C}-^{13}\text{CH}_2\text{I}$ or $\text{H}_3\text{C}-\text{CD}_2\text{I}$) are similar to that obtained using normal EtI with only a slight increase in intensity for m/z 75 or 76 in the respective cases, indicating less than 5% EtI label incorporation into PA. This result is consistent with initially added ethyl iodide initiating the carbonylation process, but not significantly participating in the catalytic cycle. When ^{13}C -ethylene was used, m/z 31, 59 and 76 ($m/z+2$ from unlabeled PA) increase substantially, indicating >94% incorporation of the double ^{13}C label from ethylene in PA.

Fig. 4(a) shows the normalized GC-MS fragmentation patterns of ethyl iodide for the corresponding cases in Fig. 3. With isotopically labeled ethyl iodide ($\text{H}_3\text{C}-^{13}\text{CH}_2\text{I}$ or $\text{H}_3\text{C}-\text{CD}_2\text{I}$), only ~40% of the product EtI (20 mmol), retains the label, comparable to the minimum amount of EtI observed transiently in Fig. 1(a). The remaining 60% of the EtI originates from unlabeled ethylene reacting with HI in steps that may or may not be catalyzed by Mo. When $^{13}\text{CH}_2=^{13}\text{CH}_2$ was used, the increased intensity at m/z 31 and 158 similarly demonstrates that $^{13}\text{CH}_2=^{13}\text{CH}_2$ reacted with iodide to yield ^{13}C -labeled EtI. Fig. 5(b) shows the normalized GC-MS fragmentation patterns of ethyl acetate for the corresponding experiments as in Fig. 3. The ethoxy group, derived from EtI, appears in fragments m/z 45($-\text{OC}_2\text{H}_5$), 73 ($-\text{COOC}_2\text{H}_5$) and the parent ion 88 when unlabeled. When using isotopically labeled EtI ($\text{H}_3\text{C}-^{13}\text{CH}_2\text{I}$ or $\text{H}_3\text{C}-\text{CD}_2\text{I}$), approximately 50% of the ethyl acetate contains a labeled ethoxy at m/z 46 or 47, corresponding to approximately 18 mmol. Although not shown, ethanol contains a similar isotopic distribution. In addition, some of the ^{13}C label from labeled EtI is unaccounted for in the detected liquid phase products, indicating either that EtI contributes significantly to coke formation or that it is transformed into gas-phase ethylene after the carbonylation reaction is complete (CO is depleted or reactor temperature is lowered). Significant conversion of EtI into ethylene while propionates were being formed would have resulted in significantly more of the EtI label being incorporated into the product than was observed.

These figures show that under reaction conditions, residual EtI and its condensation products (e.g. ethyl acetate and ethanol) have very similar isotopic distribution, indicating equilibrated interconversion. Overall, of the original labeled EtI, only less than 5% is incorporated into PA, even though large amounts are available as a reactive, equilibrated

mixture primarily of EtI and ethyl acetate. The very small extent of label incorporation into PA is therefore not because it is unavailable, but rather because EtI does not participate directly in catalyst turnover, whether fed directly or generated during reaction. In contrast, the label is incorporated nearly quantitatively from ethylene, consistent with direct incorporation of ethylene into the catalyst cycle, as in steps 6 and 8 in Fig. 2.

3.5. How is the ethyl fragment incorporated into propionic acid?

Further labeling experiments elucidate additional details regarding generation of the proposed Mo hydride (compound **D** in Fig. 2) and ethylene insertion (step 6 in Fig. 3). The Mo hydride (compound **D** in Fig. 2) is proposed to be formed from formal hydrolysis of Mo-propionyl (compound **C** in Fig. 2). Ethylene is then proposed to add directly to the Mo hydride. D₂O was used to track the formation of the Mo hydride and subsequent incorporation of ethylene. Fig. 5(a) shows the normalized GC-MS fragmentation pattern of PA using H₂O or D₂O after 2 h of reaction at 190°C. With D₂O replacing added H₂O, the reaction mixture is approximately 55% deuterons (D), with the remaining protons (H) from the acetic acid solvent. Although scrambling with H₂ was not investigated, complete scrambling with solvent would only slightly decrease the D composition in the solvent to ~50%.

Shifts in intensity for the ethyl and propionyl fragmentation patterns (m/z 27-31 and 55-59, respectively) are consistent with 26% D incorporation to form mono-deuterated propionic acid and the remainder unlabeled. Within the precision of the data, there is no evidence for significant incorporation of two D atoms into a propanoate. This level of D incorporation indicates that 1) solvent D is being incorporated into the ethyl fragment of the product, but that 2) the level of incorporation does not fully reach the D/H ratio present in the solvent. The small amount of unlabeled EtI that is expected to be incorporated into the product (5% from the above section) does not fully explain the lower-than-expected level of labeling. The corresponding GC-MS spectra of EtI exhibited increased intensity at m/z 30 and 157 (Fig. 5(b)), indicating reaction of DI with ethylene. The observed 29% D incorporation into EtI is the product of ~60% being derived from ethylene, as discussed in the previous section, and the 55% D composition in the solvent. The ethyl acetate fragmentation pattern shows a similar level of D

incorporation, consistent with the conclusions above that EtI and its condensation products are close to equilibrium after 2h at reaction conditions.

The location of D incorporation in PA can further clarify the proposed mechanism and was investigated by ^{13}C -NMR spectroscopy. Distortionless Enhancement by Polarization Transfer (DEPT-135) ^{13}C -NMR spectra of the reaction mixture (190°C for 2 h) were recorded to determine the location of the D label and to distinguish CH_2 - (negative signals) from CH_3 - groups (positive signals). Fig. 6(a) shows the spectrum using H_2O , EtI, and ethylene as reactants. A positive resonance at 8.98 and a negative resonance at 26.83 ppm are assigned to the CH_3 - and CH_2 - of propionic acid, respectively. Small shoulders at 9.04 and 26.74 ppm are assigned to the CH_3 - and CH_2 - of ethyl propionate, respectively. Fig. 6(b) shows the spectrum obtained using D_2O , EtI, and ethylene as reactants. In addition to the peaks assigned to unlabeled propionic acid, new peaks (marked as *) are a negative triplet centered at 8.79 ($-\text{CH}_2\text{D}$) and a positive triplet centered at 26.56 ppm ($-\text{CHD}-$). The 18 Hz splitting is consistent with C-D coupling constants on a labeled propionate species.[23, 24] This spectrum shows D present on either the ^1C or the ^2C of the propionate.

These spectra provide evidence to constrain possible reaction mechanisms as follows. EtI formed from the reaction of DI and ethylene will only have the label in the ^2C position, and thus oxidative addition of ^2C EtI would ultimately result in ^2C -deuterated propionic acid. In that mechanism, labeling at the ^1C position would be possible only upon elimination of HI from $\text{C}_2\text{H}_4\text{DI}$ to form $\text{CH}_2=\text{CDH}$, which then re-adds to DI to give $\text{CH}_2\text{D}-\text{CDHI}$ with a label at both the ^1C and ^2C positions. However, negligible double labeling was observed in the GM-MS, and no evidence was seen for higher order splitting in the NMR. Overall, the scrambling of the D labeling in the absence of significant double-labeled species is inconsistent with the direct involvement of EtI in steps like 2, 3, 4 and 8 of Fig. 2, which would require D labeling in only the terminal position (indicated with *). In contrast, insertion of ethylene to a $\text{Mo}[\text{D}]$ species would also result only labeling at ^2C of the ultimate product propanoate. However, making step 6 of Fig. 2 reversible through β -H elimination would scramble the position of the D label, as shown in Fig. 7. Likewise, loss of $\text{C}_2\text{H}_3\text{D}$ creates a $\text{Mo}[\text{H}]$ species where there was

once a Mo[D], which would serve to drop the D/H product ratio below the D⁺/H⁺ solvent ratio, as was indeed described in the above section.

The dominance of the ethylene insertion route also places conditions on the structure of the catalytically-active species. β -H elimination requires an unsaturated metal center and increases the coordination of the metal by one, so that coordinately saturated, kinetically stable complexes cannot undergo this type of process.[25] 7-coordinated Mo-complexes that follow the 18 electron rule have been reported for Mo(II).[26-28] On the other hand, it has also been reported that 16-electron[29] or 17-electron[30, 31] metal complexes can be stable, especially with substituted ligands. The initiating oxidative addition of EtI can take place with either Mo(CO)₅ or Mo(CO)₄ to form seven- or six-coordinate analogues of the Mo-ethyl-iodide complex **B** (as shown in Fig. 2). During catalytic turnover, β -H elimination and ethylene insertion appear to take place reversibly, scrambling the location of D labels from D₂O solvent. Since β -H elimination requires an unsaturated metal center, a six-coordinate **B** is plausibly formed in our catalytic system.

3.6 Comparison of the proposed mechanism with literature

Zoeller and coworkers reported ethylene carbonylation catalyzed by Mo(CO)₆ to form propionic anhydride.[7, 11] They proposed a free radical mechanism with dissociation of CO from Mo(CO)₆ as the rate limiting step. As given in equation 1.1, this species then attacks EtI, initiating the radical chain, and the 17 e⁻ Mo species [$\bullet$ Mo(EtCO)(CO)₅] is the predominant radical. In steps 3.1 through 3.6, I⁻ is proposed to react with [$\bullet$ Mo(EtCO)(CO)₅] and form propionyl iodide (EtCOI) and [$\bullet$ Mo(CO)₄]. In four steps, [$\bullet$ Mo(EtCO)(CO)₅] is regenerated by the addition of CO, H⁺, and C₂H₄. EtCOI reacts with the solvent – propionic acid, leading to propionic anhydride and HI (eq. 3.7).

In parallel, Roe et al. proposed a mechanism for the Rh-catalyzed, HI-promoted carbonylation of ethylene into propionic acid.[17] There, either $\text{Rh}(\text{CO})_2\text{HI}_3^-$ or $\text{Rh}(\text{CO})_2\text{HI}_2$ are key intermediates for ethylene addition to give a Rh-alkyl. Following CO migratory insertion and hydroxylation, propionic acid is formed and the Rh hydride is recovered for further reaction. The primary similarity between these proposed mechanisms and our own is the direct addition of ethylene to a metal hydride. We have demonstrated the importance of such a $\text{Mo}[\text{H}]$ intermediate by the scrambled D incorporation from D_2O . The mechanisms all initiate or promote the reaction with alkyl iodide or HI, without requiring co-catalytic alkyl iodide. We have shown that EtI is only an initiator by the absence of significant incorporation of labeled EtI into products. Likewise, we have shown that adding small amounts of ethyl iodide or other alkyl iodides (e.g. methyl iodide) does not decrease the high PA yields with respect to limiting CO.

There are two significant deviations between the Zoeller mechanism for $\text{Mo}(\text{CO})_6$ and the one proposed here. First, the mechanism proposed here does not require iodide for the elimination of acyl iodide, as in step 3.2. The absence of explicit steps for the loss and re-coordination of iodide is consistent with our observation that the catalyst is productive with much lower levels of alkyl iodide than the preferred Zoeller conditions. Secondly, the radical nature of their catalytic cycle requires that 1) the level of D incorporation into product should exactly match the level of D^+ in the solvent, and that 2) the D label would wind up in the ^2C position exclusively. Making the ethylene addition step reversible allows the D/H ratio to decrease and scrambles to the position of the D labeling. In a related concern, a mechanism invoking radical initiation via cleavage of an alkyl iodide would be retarded by the use of methyl iodide instead of ethyl iodide. Instead, we see that methyl iodide is very rapidly consumed by these catalysts for the formation of acetic acid, consistent with the more facile oxidative addition of MeI.[32]. Elimination of acetyl iodide is also expected to be more facile than for propanoyl iodide, and thus a parallel oxidative addition and reductive elimination mechanism, steps (2), (3), and (5) in Figure 2, explains why MeI, but not EtI, is significantly incorporated into the product.

4. Conclusions

Ethyl iodide is a significant promoter for propionic acid production via ethylene carbonylation, and it is seen here that propanoate yields reached near 100% for EtI loadings above 3 mmol – much lower levels than chosen by others as preferred conditions. Ethyl iodide is significantly consumed by reaction with solvent in the early stage of the reaction, but similarities in the isotopic labeling are consistent with ethyl iodide being present in a reactive equilibrium with various condensation products. Ethyl iodide is subsequently regenerated by reaction with residual ethylene and HI. The alkyl iodide promoters oxidatively add to Mo to initiate the catalytic cycle, as shown in Fig. 2. Inorganic iodide is not an effective promoter under these reaction conditions, suggesting that direct initiation by HI is less effective than initiation by alkyl iodide and that ethyl iodide formation from ethylene and HI is markedly slower than the carbonylation reaction. Using isotopic labeling, we demonstrate that ethyl iodide is not a direct participant in the catalytic cycle; it is a true promoter rather than a co-catalyst. Deuterium oxide labeling experiments show that a Mo hydride complex forms during the reaction and reacts reversibly with ethylene. Formation of propionic acid deuterated on either the ^1C or ^2C is consistent with the involvement of an unsaturated Mo complex and an equilibrium between β -H elimination and deuterated ethylene addition to the Mo hydride. The postulated unsaturated Mo hydride complex is likely stabilized by the iodide and understanding the role of the anion in future studies may be key to optimizing ethylene carbonylation processes.

Acknowledgements

The authors acknowledge the financial support of the Dow Chemical company. The authors thank Dr. Yuyang Wu at IMSERC, Northwestern University for his technical assistance in NMR. The CleanCat Core facility acknowledges funding from the Department of Energy (DE-AC02-06CH11357) used for the purchase of the gas chromatographs.

Table 1

Effects of CO, C₂H₄ and H₂ partial pressure on product yields during ethylene carbonylation catalyzed by Mo(CO)₆.^a

reactants			products ^b		
H ₂	C ₂ H ₄ (bar)	CO	propionic acid	ethyl propionate (mmol)	propanoate yield (%)
10	10	0	2.9	0.1	50 ^c
10	10	5	43.1	2.5	82
10	10	10	95.8	4.4	104
10	10	15	123.3	3.2	92
10	0	10	23.3	0.1	31 ^d
10	5	10	72.5	2.0	77
10	10	10	95.8	4.4	104
10	16	10	91.9	6.5	102
0	10	10	50.5	2.2	55
6	10	10	81.6	5.6	90
10	10	10	95.8	4.4	104
16	10	10	83.9 ^c	3.5	91

^a Reaction conditions: 1 mmol Mo(CO)₆, 1.3 mmol Bu₄PI, 76 mmol EtI, 460 mmol H₂O and 760 mmol acetic acid. 0-16 bar H₂, 0-16 bar C₂H₄ and 0-15 bar CO were sequentially pressurized at 25°C. The reaction was performed at 190°C for 5 hours under stirring speed of 900 rpm.

^b Products also include 20-30 mmol ethyl acetate, 6-8 mmol ethanol and <1 mmol DEE. Propanoate yield was calculated by the ratio of PA+EP production to the CO originally added in the reaction system, including 6 mmol CO from Mo(CO)₆.

^c CO fragments from Mo(CO)₆ limiting.

^d Ethylene fragments from EtI limiting.

^e Also observed 0.4 mmol propionaldehyde.

Table 2

Effects of iodide promoter amounts on product yields during ethylene carbonylation catalyzed by Mo(CO)_6 .^a

entry	promoters		products ^b		
	Bu ₄ PI (mmol)	EtI	propionic acid (mmol)	ethyl propionate (mmol)	propanoate yield (%)
1 ^c	0	0	44.6	-	46
2	1.3	0	47.3	-	49
3	0	76	63.1	2.4	68
4	1.3	0.6	76.0	-	79
5	1.3	3	93.1	0.1	97
6	1.3	7	94.7	0.4	99
7	1.3	13	98.4	0.8	103
8	1.3	76	95.8	4.4	104
9	1.3	143	80.0	5.9	89
10	1.3	297	77.5	6.8	87

^a Reaction Conditions: 1 mmol Mo(CO)_6 , 0-1.3 mmol Bu₄PI, 0-297 mmol EtI, 460 mmol H₂O and 760 mmol acetic acid. 10 bar H₂, 10 bar C₂H₄ and 10 bar CO were sequentially pressurized at 25°C. The reaction was performed at 190°C for 5 hours under stirring speed of 900 rpm.

^b Products also include equilibrated condensation products of EtI: ethyl acetate, ethanol, and DEE. Propanoate yield was calculated by the ratio of PA+EP production to the CO originally added in the reaction system including 6 mmol of CO from Mo(CO)_6 .

^c Additionally verified in a reactor that had no previous contact with iodide.

Table 3

Effects of different iodide promoters on product yields during ethylene carbonylation catalyzed by Mo(CO)_6 .^a

iodide	products ^b					final EtI (mmol)	propanoate yield (%)
	propionic acid	ethyl propionate	diethyl ether (mmol)	ethyl acetate	methyl acetate		
EtI	95.8	4.4	0.5	30	-	66.1	104
MeI	84.9	1.2	-	17.8	7.8	3.5 ^c	89
NaI	62.6	0.6	-	10.1	-	0.6	65

^a Reaction Conditions: 1 mmol Mo(CO)_6 , 1.3 mmol Bu_4PI , 76 mmol EtI (MeI or NaI), 460 mmol H_2O and 760 mmol acetic acid. 10 bar H_2 , 10 bar C_2H_4 and 10 bar CO were sequentially pressurized at 25°C. The reaction was performed at 190°C for 5 hours under stirring speed of 900 rpm.

^b Propanoate yield was calculated by the ratio of PA+EP production to the CO originally added in the reaction system including 6 mmol of CO from Mo(CO)_6 .

^c Also observed 5.0 mmol MeI remaining.

Fig. 1. Reactor composition during ethylene carbonylation at 190°C. 1 mmol Mo(CO)₆, 1.3 mmol Bu₄PI, 76 mmol EtI, 460 mmol H₂O and 760 mmol acetic acid. 10 bar each of H₂, C₂H₄ and CO were sequentially pressurized at 25°C, sealed, and then heated to 190°C with 900 rpm stirring. (a) Five trials terminated at 1, 2, 3, 4, and 5 h. (b) Three-hour run, after which the reactor was opened, recharged with 10 bar each H₂, C₂H₄, and CO and reacted for another 2 h at 190°C.

catalytic cycle

side reactions

Fig. 2. Possible reaction mechanisms for ethyl iodide-promoted ethylene carbonylation catalyzed by Mo(CO)_6 . Not shown are additional condensation reactions between ethyl iodide and water and acetic acid solvent to form ethyl acetate, ethanol, and diethyl ether. Here is investigated $X = \text{iodide}$, although contributions from hydride, acetate, or hydroxide cannot be completely ruled out.

Fig. 3. Portion of the GC-MS fragmentation pattern corresponding to propionic acid in the reaction mixture for different labeling scenarios of ethyl iodide and ethylene. Signal intensities are normalized by moles of propionic acid product quantified by GC-FID. Reaction conditions: 1 mmol Mo(CO)₆, 1.3 mmol Bu₄PI, 76 mmol ethyl iodide (or 1-¹³C-ethyl iodide, 1,1-*d*₂-ethyl iodide), 460 mmol H₂O and 760 mmol acetic acid. 10 bar H₂, 10 bar C₂H₄ (or ¹³C-ethylene) and 10 bar CO were sequentially pressurized at 25°C. The reaction was performed at 190°C for 2 hours at a stirring speed of 900 rpm.

Fig. 4. Portion of the GC-MS fragmentation pattern corresponding to a) ethyl iodide and b) ethyl acetate in the reaction mixture for different labeling scenarios of ethyl iodide and ethylene. Signal intensities are normalized by moles of the respective product quantified by GC-FID. Reaction conditions: 1 mmol Mo(CO)₆, 1.3 mmol Bu₄PI, 76 mmol ethyl iodide (or 1-¹³C-ethyl iodide, 1,1-*d*₂-ethyl iodide), 460 mmol H₂O and 760 mmol acetic acid. 10 bar H₂, 10 bar C₂H₄ (or ¹³C-ethylene) and 10 bar CO were sequentially pressurized at 25°C. The reaction was performed at 190°C for 2 hours at a stirring speed of 900 rpm.

Fig. 5. Portion of the GC-MS fragmentation pattern corresponding to a) propionic acid, b) ethyl iodide and c) ethyl acetate in the reaction mixture for labeled H_2O . Signal intensities are normalized by moles of the respective product quantified by GC-FID. Reaction conditions: 1 mmol $Mo(CO)_6$, 1.3 mmol Bu_4PI , 76 mmol ethyl iodide, 460 mmol H_2O (or D_2O) and 760 mmol acetic acid. 10 bar H_2 , 10 bar C_2H_4 and 10 bar CO were sequentially pressurized at $25^\circ C$. The reaction was performed at $190^\circ C$ for 2 hours at a stirring speed of 900 rpm.

Fig. 6. DEPT-135 of ^{13}C -NMR spectra of a reaction solution extract. See main text for details of separation procedure. Standard reaction conditions using (a) H_2O , or (b) D_2O . Reaction conditions: 1 mmol $\text{Mo}(\text{CO})_6$, 1.3 mmol Bu_4PI , 76 mmol EtI, 460 mmol H_2O (or D_2O) and 760 mmol acetic acid. 10 bar H_2 , 10 bar C_2H_4 and 10 bar CO were sequentially pressurized at 25°C . The reaction was performed at 190°C for 2 hours under stirring speed of 900 rpm.

Fig. 7. Illustration of β -hydrogen elimination and C₂H₄ /C₂H₃D addition to a Mo-deuteride/Mo-hydride complex, leading to normal propionic acid, 1-d-propionic acid or 2-d-propionic acid.

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