



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.

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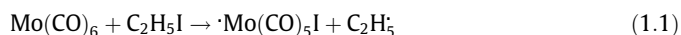
1. Introduction

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 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 hydriodic 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 hydriodic 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 Mo(CO)₅I[•] radical and ethyl radicals (1.1).



These ethyl radicals are then proposed to react with Mo(CO)₆ to form the pivotal complex [·Mo(EtCO)(CO)₅].



The Mo(CO)₅(EtCO)[•] 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

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anhydride. In follow-up studies, Zoeller et al. observed $\text{Mo}(\text{CO})_6$ 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 $[\text{Rh}(\text{}^{13}\text{CO})_2\text{I}_2]^-$, HI, and ethylene, $[(\text{CH}_3-\text{CH}_2^{13}\text{CO})\text{Rh}(\text{}^{13}\text{CO})\text{I}_2]^-$ 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 ($\text{H}_3\text{C}-^{13}\text{CH}_2\text{I}$, $\text{H}_3\text{C}-\text{CD}_2\text{I}$, $\text{H}_2^{13}\text{C}=\text{}^{13}\text{CH}_2$, 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 $\text{Mo}(\text{CO})_6$ more akin to that proposed by Roe et al. for $\text{Rh}(\text{CO})_2\text{I}_2^-$ than the radical chain proposed by Zoeller et al. for $\text{Mo}(\text{CO})_6$.

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 $\text{Mo}(\text{CO})_6$, 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 N_2 , vented, and repeated 4 times to remove gaseous and dissolved O_2 . 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 H_2 (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, C_2H_4 or H_2 being charged in the headspace of the reactor. Based on Henry's law constants for H_2O [19], 0.7 mmol of CO, 3.5 mmol of C_2H_4 and 0.6 mmol of H_2 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 h, 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 \times 0.2 mm \times 0.4 μm) in the CleanCat core facility. Propanoate yield was calculated relative to added CO, including CO present in $\text{Mo}(\text{CO})_6$, 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 D_2O , 99 atom% ^{13}C -ethylene ($^{13}\text{CH}_2=\text{}^{13}\text{CH}_2$), $1\text{-}^{13}\text{C}$ -ethyl iodide ($\text{CH}_3-\text{}^{13}\text{CH}_2-\text{I}$), and $1,1\text{-}d_2$ -ethyl iodide ($\text{CH}_3-\text{CD}_2-\text{I}$) were used to replace water, ethylene and ethyl iodide, respectively. An Agilent 7975C GC-MS-FID and a VF-WAX column (30 m \times 0.25 mm \times 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 ^{13}C nuclear magnetic resonance (NMR) and DEPT-135 (distortionless enhancement by polarization transfer) spectra were recorded with a Bruker Avance-III spectrometer (125 MHz for ^{13}C) 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 $\text{Mo}(\text{CO})_6$ and EtI as a separate phase. The aqueous phase was extracted with 200 cm^3 hexanes to remove water-miscible TBPI. The organic phase was concentrated by rotary evaporation and dissolved into $\text{DMSO}-d_6$ for ^{13}C 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 are formed after reaction and isolated by filtration before GC analysis. X-ray diffraction of these precipitates is most consistent with graphitic coke (see Supporting Information Fig. S1), but the presence of insoluble Mo species cannot be ruled out completely. In the absence of $\text{Mo}(\text{CO})_6$, neither propionates nor coke was formed.

In the absence of added CO, PA is still observed, corresponding to incorporation of approximately half of the CO in the added $\text{Mo}(\text{CO})_6$, 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

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