Chemical Fixation of CO$_2$ to Acrylates Using Low-Valent Molybdenum Sources

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In cooperation with Charles Stark Draper Labs

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Presentation Outline

• Deriving acrylates from CO$_2$: How and why

\[ \text{Propene} + \text{CO}_2 \xrightarrow{[M]} \text{Acrylate} \]

• Assessing viability of chemical catalysis approach.

• Method for enhanced throughput catalyst screening

• Perspectives for the future.
Benefit to the Program

- This project pinpoints the critical catalyst features necessary to promote carbon dioxide conversion to acrylate, validate the chemical catalysis approach, and develop an enhanced screening method identification of active molybdenum catalysts targets. This methodology will contribute to the goal ensuring 99 percent storage permanence by fixing CO$_2$ in stable products for indirect storage.
Project Overview: Goals and Objectives

• Identify features for activation of molybdenum in CO₂ and ethylene coupling to acrylates.
  – Probe mechanism of zerovalent molybdenum complexes to determine the factors that control the reaction rate. (Complete)

• Validate reductive acrylate elimination
  – Use active species to assay the potential for reductive acrylate extrusion. (Complete)

• Develop and utilize an enhanced screening method for activity identification in acrylate formation.
Guiding Motivations

Present & Future of Acrylate Synthesis

**Proposed:**

\[ \text{Proposed: } \text{CH}_2=\text{CH}_2 + \text{CO}_2 \xrightarrow{[M]} \text{CH}_2=\text{CH}-\text{CO}_2\text{H} \]

**Current:**

\[ \text{Current: } \text{CH}_2=\text{CH}_2 + \text{O}_2 \xrightarrow{\text{Bi}_2(\text{MoO}_4)_3 \text{ - H}_2\text{O}} \text{CH}=\text{CH}_2 \xrightarrow{V_x\text{O}_y\text{Mo}_z} \text{CH}_2=\text{CH}-\text{CO}_2\text{H} \]

- 370 °C
- 270 °C

acrolein

370 °C

270 °C
Guiding Motivations

Present & Future of Acrylate Synthesis

**Proposed:**

\[ \text{current process} + \text{CO}_2 \xrightarrow{[M]} \text{acrylic acid} \]

**Current:**

\[ \text{propylene} + \text{O}_2 \xrightarrow{\text{Bi}_2(\text{MoO}_4)_3, 370^\circ \text{C}} \text{acrolein} \xrightarrow{\text{V}_x\text{O}_y\text{Mo}_z, 270^\circ \text{C}} \text{acrylic acid} \]

- Currently produce ~5 M tons of acrylic acid/yr (SAP largest single use)
- Using CO\(_2\) as carbon source with same net carbon requirements of the current process would equate to 3-8 M tons of CO\(_2\) (up to 1 billion gal of gasoline)
- Economic Value and Industrial Investment: Propylene (~70 ct/lb); Ethylene (~55 ct/b)

Which Metals Could Work?

Prior Art-Molybdenum (NETL-Project)

\[
\begin{align*}
P & = \text{PMe}_3, \text{PMe}_2\text{Ph}, \\
P(\text{OMe})_3, \text{P(OEt)}_3
\end{align*}
\]

Galindo, A.; Pastor, A.; Pérez, P.J.; Carmona, E. Organometallics 1993, 12, 4443.

Prior Art-Nickel

\[
\begin{align*}
\text{[Ni]} + \text{P} &\xrightarrow{\text{CO}_2, \text{C}_2\text{H}_4} \\
\text{P} &\xrightarrow{\text{Ni}} \text{O} \text{C} \text{O} \\
\text{P} &\xrightarrow{\text{Ni}} \text{O} \text{C} \text{H}
\end{align*}
\]

Molybdenum

Catalysis Needs

- Molybdenum is quite capable of reactions 1, 2 & 3 individually
- Little is known about what makes molybdenum the “rare” success
- Identification of successful single-site molybdenum activity requires intensive fine chemistry assay
Molybdenum

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First New CO₂-Ethylene Acrylate in Decades

Mechanism of Action

\[ \frac{k(C_2H_4)}{k(C_2D_4)} = 1.2(2) \]

\[ \Delta S^+ = 1(6) \text{ eu; } \Delta H^+ = 24(3) \text{ kcal/mol} \]

\( ^1H \text{ NMR: } \delta 0.25, \text{ m, } C_2H_4 \)

\( ^31P \text{ NMR: } \delta 64.7, \text{ d, 6.1Hz} \)

\( 95.3, \text{ t, 6.1Hz} \)

\( ^{13}C \text{ NMR: } \delta 193.6, \text{ dt, 15, 28Hz} \)

IR(KBr) \( \nu_{C=O} = 1700 \text{ cm}^{-1} \)

Mechanism of Action

Computational Modeling

Free Energies of Reaction Species
Viability of Elimination

Direct Elimination

Overall thermodynamically feasible in solvent/slurry.

Oxidation state = 2

Oxidation state = 0
Viability of Elimination

Direct Elimination

...but $pK_a \sim 30-35$

Overall thermodynamically feasible in solvent/slurry.

$pK_a \sim 13$
Viability of Elimination

Indirect Elimination-Base

\[
\text{Na-base or Li-base} \quad \xrightarrow{\text{Molecule}} \quad \text{Product} \quad \xleftarrow{\text{Compound}}
\]
Viability of Elimination

**Indirect Elimination-Base**

- Presence of carbon monoxide actually enables this process, not inhibit it
- Metal-carbonyls are frequently activated by photolysis for catalysis
- Probably the best lead for molybdenum induced acrylate formation

**Ligand Induced Elimination**

- Presence of carbon monoxide actually enables this process, not inhibit it
- Metal-carbonyls are frequently activated by photolysis for catalysis
- Probably the best lead for molybdenum induced acrylate formation
Need for Rate Enhancement

**Enhanced Activity Screening Method**

- Formate, propionate, and acrylate produced from single reaction

Need for Rate Enhancement

Enhanced Activity Screening Method

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Need for Rate Enhancement

Enhanced Activity Screening Method

- Formate, propionate, and acrylate produced from single reaction

## Need for Rate Enhancement

### Activity Results—8 New Active Catalyst Targets

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Observation</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bis(diphenylphosphino)ethyl-phenylphosphine]</td>
<td>Clear acrylate production detected</td>
<td>$5.2 \times 10^{-5}$ s$^{-1}$</td>
</tr>
<tr>
<td>[bis(dianisolephosphino)ethyl-phenylphosphine]</td>
<td>Clear acrylate production detected:</td>
<td>$2.54 \times 10^{-5}$ s$^{-1}$</td>
</tr>
<tr>
<td>[bis(di-m-xylyl-phosphino)ethyl-phenylphosphine]</td>
<td>Clear acrylate production detected</td>
<td>$4.15 \times 10^{-5}$ s$^{-1}$</td>
</tr>
<tr>
<td>[bis(di-p-fluorophenyl-phosphino)ethyl-phenylphosphine]</td>
<td>Clear acrylate production detected:</td>
<td>$3.2 \times 10^{-5}$ s$^{-1}$</td>
</tr>
<tr>
<td>[bis(di-p-trifluoroethyl-phenyl-phosphino)ethyl-phenylphosphine]</td>
<td>Clear acrylate production detected:</td>
<td>$4.05 \times 10^{-4}$ s$^{-1}$</td>
</tr>
<tr>
<td>[bis(dipyrrrolephosphino)ethyl-phenylphosphine]</td>
<td>No acrylate formation detected</td>
<td></td>
</tr>
<tr>
<td>1,1,1-Tris(diphenylphosphinomethyl)ethane</td>
<td>No acrylate formation detected</td>
<td></td>
</tr>
<tr>
<td>Methyl substituted 1,4,7-Triazacyclononane</td>
<td>No acrylate formation detected</td>
<td></td>
</tr>
<tr>
<td>[bis(di-tertbutil-phosphino)ethyl-phenylphosphine]</td>
<td>Preliminary data suggest acrylate formation, additional characterization on-going</td>
<td>TBD</td>
</tr>
<tr>
<td>[bis(dicyclohexylphosphino)ethyl-phenylphosphine]</td>
<td>Preliminary data suggest acrylate formation, additional characterization on-going</td>
<td>TBD</td>
</tr>
<tr>
<td>N,N’-(2,4,6-Trimethyl)-imidazolium</td>
<td>Preliminary data suggest acrylate formation, additional characterization on-going</td>
<td>TBD</td>
</tr>
<tr>
<td>N,N’-(2,6-Diisopropylphenyl-imidazolium)</td>
<td>Preliminary data suggest acrylate formation, additional characterization on-going</td>
<td>TBD</td>
</tr>
<tr>
<td>N-Methyl-triazacyclononane</td>
<td>No acrylate formation detected</td>
<td></td>
</tr>
<tr>
<td>1,3-Bis(di-tert-butylphosphinomethyl)benzene</td>
<td>No acrylate formation detected</td>
<td></td>
</tr>
<tr>
<td>N,N’-Dimethyl-imidazolium</td>
<td>No acrylate formation detected</td>
<td></td>
</tr>
</tbody>
</table>
Accomplishments to Date

- Discovery of rare metal complex for CO\textsubscript{2} and ethylene coupling to acrylates.
- Identified the tridentate structural features that best enable CO\textsubscript{2} utilization.
- Developed a basic profile for CO\textsubscript{2} reduction pathway.
- Discovery of base and ligand induced reductive elimination pathways for acrylate removal.
- Established an enhanced throughput screening method using sodium triethylborohydride for assessment of acrylate formation activity in molybdenum.
Future Plans

- Identify activation methods for CO or other ligand induced reductive elimination method.
- Complete screening of metal ligand pairs to optimize acrylate formation rate.

(Mo Targets Outside Current NETL Project)
- Heterogenize Mo catalyst as Nanoparticles
- Alternate Product Scope
  - Formic acid, propionic acid
  - Cyclic anhydrides
Appendix
This program is run under the auspices of Wesley Bernskoetter, Assistant Professor of Chemistry at Brown University as the principle investigator. Dr. Bernskoetter and his graduate students are part of the chemistry department, and as such, have access to the facilities of Brown and its chemistry department. In addition to the Brown, the project team has access to computational chemistry support and additional chemical and engineering support, as required, through its collaboration with Draper Laboratory.
Gantt Chart
Bibliography

Peer Reviewed Publications

