CONTINUATION REPORT
New Tools for CO₂ Fixation by Homogeneous Catalysis
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Abstract

In the first 8 months of this grant, the PI and his team have developed new hydrogenation catalysts for CO₂ fixation, screened a series of ligands for their ability to dissolve in CO₂, and invented a new and environmentally benign system for recovering and recycling homogeneous catalysts using CO₂ and liquid polymers. The team has also begun work on two projects: a) the evaluation of the effect of secondary interactions between ligands and CO₂ on the insertion of CO₂ into M-H bonds, and b) the design and testing of promoters or catalysts for the insertion of CO₂ into C-H bonds. Ongoing research is primarily focusing on these last two projects.

Results to Date:

Bifunctional phosphines – Lewis basic

In the search for an aromatic phosphine that is more CO₂-soluble than PPh₃, the Jessop group has prepared several new phosphines and several known phosphines. The working hypothesis, as presented in the proposal, was that triarylphosphines which incorporate Lewis basic secondary functional groups would be more soluble than triarylphosphines without such additional functional groups. The solubility of most of the ligands prepared by the Jessop group has been measured in CO₂ by the group of Dr. Eric Beckman at the University of Pittsburgh. Despite literature¹ speculation to the contrary, the ligand Ph₂PC₆H₄pCO₂Me, one of those prepared and tested, is not more soluble in CO₂ than is PPh₃; in fact the solubility of the former is very low indeed. On the other hand, the strategy of using an aromatic heterocycle in place of the phenyl rings was successful; the ligand tris(2-furyl)phosphine was found to be more soluble in scCO₂ than is PPh₃. Phosphines which have been synthesized but not yet tested for CO₂ solubility include structures **1** and **2** below. The former incorporates a peracetylated sugar, a feature that takes the strategy of ester group incorporation to an extreme. The latter is a phosphine that, although it is technically a trialkylphosphine, is known to have similar electronic and steric properties to triphenylphosphine. The hypothesis is that its

solubility properties should be very similar to entirely saturated ring compounds, which are very soluble in CO₂, even though its ligand properties more closely match those of aromatic phosphines. We look forward to receiving the solubility data for these two remaining phosphines.

Bifunctional phosphines – Brønsted acidic

Current theory in the fields of ketone² and CO₂^{3,4} hydrogenation suggest that the presence of Brønsted-acidic or hydrogen bond-donating groups proximate to a metal hydride site assists in the hydrogenation of C=O double bonds. While this has been substantially established in the ketone hydrogenation literature, it has remained speculation in the CO₂ fixation literature. The plan in this portion of the research is to prepare phosphines (PR₃) with Brønsted-acidic groups (contained within the R groups), prepare and characterize analogues of RuH₂(PR₃)₃, and measure the equilibrium and rate of CO₂ insertion into the Ru-H bond as a function of the nature and structural placement of the Brønsted-acidic group. The equilibrium and kinetic measurements with the parent complex RuH₂(PPh₃)₃ are currently underway, and the preparation of the analogue complexes will start at the completion of that stage.

Development of new hydrogenation catalysts

The application of homogeneous catalysis is hampered, at least partly, by the over-reliance on complexes of the extremely expensive platinum-group metals. A study⁵ of the catalytic activity of combinations of phosphine and amine ligands with other transition metal salts as potential CO₂ hydrogenation catalysts (cf. equation 1) has found many that have at least moderate catalytic activity and a few, including NiCl₂/dcpe and FeCl₃/dcpe that have fairly high activity (dcpe = 1,2-bis(dicyclohexylphosphino)ethane). The isolated complex NiCl₂(dcpe) was then found to catalyze the hydrogenation of CO₂ to formic acid in 4,400 turnovers (mol product per mol catalyst). This activity is three orders of magnitude greater than the activity of the only previously-known catalyst⁶ outside of the platinum group metals.

Catalysts for the hydrogenation of CO₂ to oxalic acid or oxalate salts proved to be much more elusive. At first, assay method development was necessary because oxalate anion is notoriously difficult to detect spectroscopically and distinguish from formate. The student researcher was able to identify conditions suitable for the in-situ methylation

of oxalate anion by dimethylsulfate to dimethyloxalate, which was then detectable by gas chromatography. With this assay method, it was possible to show, for the first time, that catalysts having high activity for the hydrogenation of CO₂ to formate anion do not simultaneously produce detectable quantities of oxalate anion. However, the catalyst prepared in-situ from tricyclohexylphosphine and either PdCl₂(MeCN)₂ or tris(dibenzylideneacetone)-dipalladium(0) was found to be capable of producing small quantities of oxalate anion at 100 °C (equation 2). Any variation of the ligand choice suppressed the activity. Denise and Sneed reported the detection of traces of diethyloxalate in a similar reaction in ethanol solvent at 120 °C.⁷

The co-hydrogenation of CO₂ and aromatic amines catalyzed by a Pd/W cluster was found to give alkylformamides via simultaneous hydrogenation of C=C, C=N and C=O double bonds (equations 3 and 4). We are currently optimizing the conditions.

Development of new catalysts for CO₂ insertion reactions

The research group has also been investigating the insertion of CO₂ into C-O and C-H bonds.

Chiral catalysts are currently being tested for the asymmetric insertion of CO₂ into butadiene monoxide (equation 5). The only previously reported catalysts for this reaction have been achiral.⁸ Active asymmetric catalysts have now been identified, but the enantioselectivity of these is still being evaluated.

Nearly half of the ongoing effort is currently directed at the development of promoters for the insertion of CO₂ into C-H bonds. At first, we are looking at electron withdrawing metal fragments, of which the most obvious is Cr(CO)₃, to act as stoichiometric activators of the C-H bonds either on aromatic rings or proximate to these (eg. equation 6 where B is a base known to not react with CO₂, eg. 1,8-diazabicyclo[5.4.0]undec-7-ene). Either in parallel or afterwards, we will be performing a search for complexes capable of catalyzing this reaction, based upon a cycle involving arene coordination, deprotonation, electrophilic attack by CO₂, and arene dissociation.

The key here is to identify a metal fragment capable of binding the arene and activating it but not likely to be irreversibly bound to the carboxylate product.

Utilization of CO₂ in combination with new solvents

In work partly funded by this grant, the group has discovered a new method for recovering and recycling homogeneous catalysts without the use of volatile or halogenated organic solvents. The combination of supercritical CO₂ and liquid polymer (poly(ethylene glycol)) gives a biphasic solvent system which is environmentally benign, nontoxic, extremely inexpensive in materials, and very efficient for catalyst recycling. The method was demonstrated with a simple hydrogenation of olefins. Application of this method to other reactions, including fixation of CO₂, is underway. The CO₂-fixation portion of the research will continue to be funded by this grant while the other reactions will be funded by another grant. The initial communication⁹ received press coverage in *Chemical and Engineering News*¹⁰ and a full page news commentary in *Nature*.¹¹

Future Work:

As mentioned above, the continuing and future work to be funded in the remaining year is in the following areas, with approximate level of effort shown as percentages.

40% - evaluation of the promotion of CO₂ insertion into C-H bonds

40% - evaluation of the effect of Brønsted-acidic groups on CO₂ insertion into Ru-H bonds

10% - evaluation of enantioselectivity of catalysts for CO₂ insertion into epoxides

10% - wrap up and publication of the aromatic amine hydrogenation and the liquid polymer projects.

All of these are continuations of the projects described in the results-to-date section. It is expected that the last three of these four projects can be completed in the time remaining. The C-H bond activation project, however, is likely to be a substantial undertaking. Despite this, it is certainly worthwhile because it represents an important challenge to CO₂ activation and has both fundamental importance and practical application. We fully expect to be able to produce meaningful and important data on that project in the time remaining, whether or not it will be possible to bring the project to completion.

References:

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- (2) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97-102.
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Articles citing this grant published/in press since the start of this funding period

1. P. Munshi, D. J. Heldebrant, E. P. McKoon, Patrick A. Kelly, C.-C. Tai, P. G. Jessop, "Formanilide and Carbanilide from Aniline and Carbon Dioxide" *Tetrahedron Letters* (2003) **44**, 2725-2727.
2. P. G. Jessop, "Homogeneous Catalysis and Catalyst Recovery using Supercritical Carbon Dioxide and Ionic Liquids" *J. Synth. Org. Chem.* (2003), **61**, 484-488.
3. P. G. Jessop, "Asymmetric Catalysis in Supercritical Fluids" in *Drug Delivery and Supercritical Fluid Technology*, P. York, B. Kompella, B. Y. Shekunov (eds.), Marcel Dekker, New York, in press.
4. D. J. Heldebrant, P. G. Jessop, "Poly(Ethylene Glycol) and Supercritical Carbon Dioxide: A Benign Biphasic Solvent System for Recycling of Homogeneous Catalysts" *J. Am. Chem. Soc.* (2003) **125**, 5600-5601.

Articles in "submitted" status

5. A. D. Getty, C.-C. Tai, J. C. Linehan, P. G. Jessop, M. M. Olmstead, A. L. Rheingold, "Hydrogenation of Carbon Dioxide Catalyzed by Ruthenium Trimethylphosphine Complexes: A Mechanistic Investigation using High-Pressure NMR Spectroscopy" *submitted*.
6. C.-C. Tai, T. Chang, B. Roller, P. G. Jessop, "High Pressure Combinatorial Screening of Homogeneous Catalysts: Hydrogenation of Carbon Dioxide", *submitted*.

Budget Changes

The attached budget for the second year of the grant is changed from the original in the following ways:

1. Salary for the PI is removed (the PI is now in a 12-month position and can no longer accept summer salary from DOE).

2. Salary for the graduate students is decreased from 3 students in the summer to only 2, because of the winding down of the Jessop group at the University of California in favor of the group at Queen's University.
3. The domestic travel expenses are increased to allow travel of the PI and students between the two universities (Queen's and UCDavis).
4. An amount for foreign travel has been added to allow the PI or a student to attend an international conference during the second year, probably the ACHEMA "Green Solvents for Synthesis" conference in Germany in 2004.
5. The supplies/materials line has been increased slightly to allow for expected costs in waste disposal.
6. Other lines such as amount of indirect costs, recharges, fee remission, etc. have been changed as needed because of the changes described in items 1-5.