

Homogeneous Catalysis

Catalytic Formation of Acrylate from Carbon Dioxide and Ethene

Coen Hendriksen,^[a] Evgeny A. Pidko,^[b, c] Gang Yang,^[b] Benjamin Schöffner,^[d] and Dieter Vogt^{*[a]}*Dedicated to Professor Willi Keim on the occasion of his 80th birthday*

Abstract: With regard to sustainability, carbon dioxide (CO₂) is an attractive C1 building block. However, due to thermodynamic restrictions, reactions incorporating CO₂ are relatively limited so far. One of the so-called “dream reactions” in this field is the catalytic oxidative coupling of CO₂ and ethene and subsequent β-H elimination to form acrylic acid. This reaction has been studied intensely for decades. However up to this date no suitable catalytic process has been established. Here we show that the catalytic conversion of ethene and CO₂ to acrylate is possible in the presence of a homogeneous nickel catalyst in combination with a “hard” Lewis acid. For the first time, catalytic conversion of CO₂ and ethene to acrylate with turnover numbers (TON) of up to 21 was demonstrated.

Research has increasingly focused on the use of renewable materials for the production of industrially important chemicals as an alternative for the use of fossil carbon feedstocks.^[1] An interesting carbon source is CO₂, a cheap, non-toxic and abundantly available C1 building block.^[2] At this moment, the industrial use of CO₂ remains restricted to a number of processes (e.g. formation of urea, methanol, benzoic acid and derivatives, certain tertiary carboxylic acids (Koch acids) and (poly) carbonates).^[3] In general, examples of thermodynamically feasible reactions incorporating CO₂ into organic molecules are quite limited so far.^[4] A very interesting and attractive example would be the formation of acrylates from alkenes, for example, ethene, and CO₂, a so called “dream reaction”,^[5] where 62% of

the mass of the organic molecule would originate from CO₂. Currently, the production of acrylic acid relies on the oxidation of propene with molecular oxygen on Mo-oxide catalysts.^[6] Given the fact that there is an increasing demand for propene to produce polypropylene, replacement by ethene for the production of acrylates is desirable. Furthermore, the sustainability of the process can also benefit from the use of bio-ethene derived from bio-ethanol.^[7] However, up to date, no truly catalytic formation of acrylates from CO₂ and C₂H₄ has been achieved.

Initial studies on the nickel-mediated oxidative coupling of CO₂ and olefins to form nickelalactones were reported in the 1980s.^[8] These nickelalactones are thought to be intermediates in proposed catalytic acrylate-producing reactions.^[9] However, nickelalactones do not easily undergo β-H elimination due to conformational constraint of the five-membered ring, which prevents agostic β-H interactions with the nickel metal center. Extensive theoretical studies on β-H elimination of nickelalactones indicated that dissociation of the Ni–O bond to relieve the ring strain could facilitate β-H elimination.^[10] Several research groups have experimentally investigated the possibility of this proposal by the reaction of nickelalactones with alkyl halides,^[11] strong bases,^[12] or Lewis acids.^[13] Although in stoichiometric reactions acrylates were formed in moderate to good yield, the catalytic cycle could not be closed. Recently, by using a complicated process scheme involving a strong base as a promoter, turnover numbers of up to 10 have been obtained in the oxidative coupling of CO₂ and ethene to form acrylate.^[12] To prevent carbonate formation, the reactive gas had to be switched from CO₂ to ethene and back 18 times with sequential addition of stoichiometric amounts of base. It is obvious that this method is not practical. Thus, the major challenges remain: efficient formation of the active catalytic species and β-H elimination using benign reagents to complete the catalytic cycle.

We report here on our strikingly simple concept that allowed us for the first time to achieve real catalytic turnover. Our consideration was that a “hard” Lewis acid should be able to compete with the intramolecular binding of the formed nickel carboxylate in the nickelalactone and allow β-H elimination to occur (Figure 1).

The ability of a hard Lewis acid to facilitate β-H elimination from the Ni-lactone was investigated first in parallel by DFT calculations at the M06L/6-31 + G(d,p) level of theory and in stoichiometric reactions.^[14] DFT calculations indicate that the presence of Li⁺ decreases the overall free energy barrier (G[‡])

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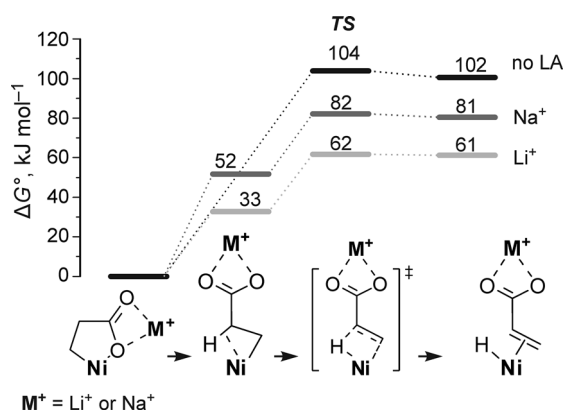


Figure 1. The transition state for β -H elimination in chlorobenzene can be lowered by “hard” Lewis acids. Pre-activation of the nickelalactone by a Lewis acid allows for σ C–H complex formation which can undergo β -H elimination. The activation Gibbs free energy for β -H elimination of a nickelalactone in the absence of a Lewis acid is $G^\ddagger = 104 \text{ kJ mol}^{-1}$, which is reduced in the presence of Na^+ or Li^+ cations to $G^\ddagger = 82 \text{ kJ mol}^{-1}$ and $G^\ddagger = 62 \text{ kJ mol}^{-1}$ respectively.

for β -H elimination (Figure 1). For comparison, the effect of the “softer” Na^+ is less pronounced; a reduction of the G^\ddagger of 22 kJ mol^{-1} compared to 42 kJ mol^{-1} for Li^+ was calculated. The optimized structures of the intermediates and transition states involved can be found in the Supporting Information (Figure S1 and Table S1).

In order to provide proof of principle we chose lithium iodide as a simple and readily available reagent, combining the very “hard” cation Li^+ and the “soft” iodide. The ability to promote the decomposition of the Ni–lactone to form the acrylate was tested in stoichiometric reactions for LiI. For this purpose Ni–lactone $[(\text{dppe})\text{Ni}(\text{C}_3\text{H}_4\text{O}_2)]$ (**1**) was used because it is stable and can easily be synthesized.^[9] Thorough screening of the reaction conditions (solvent, salt) revealed that lithium acrylate was formed in up to 73% yield after **1** was reacted with five equivalents of LiI in dichloromethane (CH_2Cl_2) for 24 h (Table 1, entry 1). As the only by-product, lithium propionate was formed. Complex **1** is completely transformed into $[(\text{dppe})\text{NiI}_2]$. Formation of propionate could be prevented by the addition of an excess of triethylamine (Et_3N), which increased the formation of lithium acrylate to 95% (Table 1,

Table 1. Decomposition reaction of complex 1 with MX salts in CH_2Cl_2 . ^[a]			
Entry	MX	Base	Yield [%]
1	LiI	–	73 ^[b]
2	LiI	Et_3N	95 ^[b]
3	LiBr	–	8 ^[c]
4	LiCl	–	3 ^[c]
5	NaI	–	4 ^[c]

[a] General reaction conditions: 25 μmol $[(\text{dppe})\text{Ni}(\text{C}_3\text{H}_4\text{O}_2)]$; 125 μmol MX; 1.25 mmol base; 1 mL dichloromethane; 20 h, 25 °C. [b] Determined by ^1H NMR spectroscopy with an internal standard. [c] Determined by GC with an internal standard.

entry 2). Probably the formation of propionate is due to the protonation of the Ni–C(alkyl) bond in **1** by HI produced on β -H elimination in the presence of LiI; addition of Et_3N prevents the buildup of HI. Complex **1** is easily protonated by strong acids resulting in the formation of propionate.

With an efficient and simple stoichiometric method in hand for the formation of lithium acrylate from **1**, we set out to design a closed catalytic cycle. The following considerations were taken into account: Based on previous studies^[8a–c, 12] and our own experience, we anticipated that a strongly basic, preferably chelating ligand would be needed for the oxidative coupling of ethene and CO_2 . Therefore 1,2-bis(dicyclohexylphosphino)ethane (DCPE) was chosen for initial tests, together with bis(1,5-cyclooctadiene)nickel ($[(\text{Ni}(\text{cod})_2)]$) as catalyst precursor. Together with LiI to facilitate the β -H elimination this would lead to Li–acrylate as the product and the $[(\text{dcpe})\text{NiHI}]$ complex. In order to regenerate the active catalyst species by reductive elimination of HI, a weak base should suffice, similar to Ni-catalyzed Heck-type reactions.^[15] To this end triethylamine was initially chosen. As solvent chlorobenzene (PhCl) was selected, as it facilitates the coordination of weakly binding substrates to metal complexes. At 50 °C under a pressure of 10 bar ethene and 20 bar CO_2 the other reaction parameters were systematically studied (Table 2). In the absence of LiI and base no lithium acrylate was detected (Table 2, entry 1). However, with 25 equivalents of LiI, under the described reaction conditions, lithium acrylate was formed in small quantities with 20% of lithium propionate as side product (Table 2, entry 2). To regenerate the active species and to prevent the formation of lithium propionate, Et_3N was added to abstract HI formed after β -H elimination. This indeed increased the yield of lithium acrylate and inhibited the formation of lithium propionate (Table 2, entry 3). However the reaction mixture turned purple, hinting at the formation of $[(\text{dcpe})\text{NiI}_2]$ as an inactive species. The for-

Table 2. Optimization of the catalytic formation of lithium acrylate from CO_2 and C_2H_4 . ^[a]				
Entry	MX	Red.	Base	TON ^[b]
1	–	–	–	0
2	LiI	–	–	< 1
3	LiI	–	Et_3N	1
4	LiI	Zn	–	2
5	LiI	Zn	Et_3N	8
6	–	Zn	Et_3N	0
7	–	–	Et_3N	0
8	NaI	Zn	Et_3N	< 1
9	LiBr	Zn	Et_3N	1
10	LiCl	Zn	Et_3N	< 1
11	LiI	Zn	DIPEA	1
12	LiI	Zn	K_2CO_3	2
13	LiI	Zn	C_5CO_3	0

[a] General reaction conditions: 50 μmol $[(\text{Ni}(\text{cod})_2)]$; 50 μmol DCPE; 1.25 mmol MX; 2.5 mmol base; 2.5 mmol Zn; 2 mL chlorobenzene; 10 bar C_2H_4 ; 20 bar CO_2 ; 72 h, 50 °C. [b] Determined by ^1H NMR spectroscopy with an internal standard.

mation of purple $[(dppe)Ni]_2$ was already observed earlier in the stoichiometric studies. To reduce $[(dcpe)Ni]_2$ back to $[(dcpe)Ni]^0$, Zn-dust was added as a reducing agent (Table 2, entry 4). Even in the absence of base, this increased the TON but the combination of base and reducing agent lead to the first real catalytic turnover ever reported for this reaction. Lithium acrylate was formed with a turn over number (TON) of 8 (Table 2, entry 5). Without Lil, neither Zn-dust nor base led to the formation of acrylate (Table 2, entries 6 and 7).

Subsequently the nature of the alkali halide and the base were varied. As anticipated the TON went down for the Li halides from iodide to bromide, to chloride (Table 2, entries 9 and 10). Noteworthy was that also NaI gave some, although low turnover (entry 8). The other Na halides showed no effect at all. Other bases typically used in Ni-catalyzed Heck-type reactions such as diisopropylethylamine (DIPEA), K_2CO_3 , and Cs_2CO_3 were less efficient than Et_3N (Table 2, entries 11–13).^[15] Therefore, the combination of Lil and Et_3N was used for all further catalysis experiments.

The amounts of Lil, Zn and Et_3N were varied from the initially chosen ones. Only increasing the amount of Zn-dust had a minor positive effect on the TON (see Table S2 in the Supporting Information, entries 2, 4, and 6). On the other hand decreasing the amount of either of those reagents had an overall negative effect on the TON (see Table S2, entries 1, 3, and 5). Reducing the reaction time to 24 h still gave a TON of 6, implying that the reaction is faster in the beginning (see Table S2, entries 7 and 8). Without Zn as reducing agent, the TON reached 1 after 24 h, similar to the reaction after 72 h (Table 2, entry 3).

With optimized catalysis conditions established for the DCPE ligand, in the following the chelate ring size was systematically varied. A whole variety of ligands was screened under these reaction conditions and only the ligands given in Table 3 proved to be effective. As previously reported, the formation of the nickelalactone intermediate is considered to be favored by strongly electron-donating amine and phosphine ligands.

For the DCPM ligands, an increase of the chelate ring size^[16] and the bite angle had a positive effect on the Ni-catalyzed reaction, with 1,3-bis(dicyclohexylphosphino)propane (DCPP) providing the best results for the reaction in the presence of Zn (Table 3, entry 6). However, with DCPP and 1,4-bis(dicyclohexylphosphino)butane (DCPB) TONs of 4 and 5, respectively, were achieved also without Zn as a reducing agent (Table 3, entries 5 and 7). It appears that those ligands suppress the formation of inactive $[(ligand)Ni]_2$. Next, the effect of the CO_2 and C_2H_4 pressure was investigated independently. The ethene pressure was increased and the CO_2 pressure decreased (Table 3, entries 9–12). From the results presented in Table 3, it can be deduced that the ethene/ CO_2 pressure ratio has a significant influence on the formation of lithium acrylate with DCPP as ligand (Table 3, entries 11 and 12). The TON was improved to 16 by increasing the ethene pressure (Table 3, entry 11); notably, this was achieved without Zn as reducing agent, which considerably simplifies the procedure. Thus, the choice of ligand and a higher ethene/ CO_2 pressure ratio have a large beneficial effect on the formation of acrylate and significant

Table 3. Catalytic formation of lithium acrylate from CO_2 and C_2H_4 with ligand and CO_2/C_2H_4 ratio variation.^[a]

$$\begin{matrix} \text{PR}_2 \\ | \\ \text{---} \\ | \\ \text{PR}_2 \end{matrix} \begin{matrix} \text{DCPM } n = 0 & R = \text{Cy} \\ \text{DCPE } n = 1 & R = \text{Cy} \\ \text{DPPE } n = 1 & R = \text{Ph} \\ \text{DCPP } n = 2 & R = \text{Cy} \\ \text{DCPB } n = 3 & R = \text{Cy} \end{matrix}$$

Entry	Ligand	Red.	C_2H_4 (bar)	CO_2 (bar)	TON ^[c]
1	DCPM	–	10	20	< 1
2	DCPM	Zn	10	20	1
3	DCPE	–	10	20	1
4	DCPE	Zn	10	20	8
5	DCPP	–	10	20	4
6	DCPP	Zn	10	20	9
7	DCPB	–	10	20	5
8	DCPB	Zn	10	20	6
9	DCPE	–	30	10	3
10	DCPE	Zn	30	10	8
11	DCPP	–	25	5	16
12	DCPP	Zn	25	5	14
13	DCPP	Zn	25	5	21 ^[b]
14	DPPE	–	25	5	< 1
15	DPPE	Zn	25	5	8

[a] General reaction conditions: 50 μmol $[Ni(cod)_2]$; 50 μmol ligand; 1.25 mmol Lil; 2.5 mmol Et_3N ; 2 mL chlorobenzene; 2.5 mmol Zn; 72 h, 50 °C. [b] 25 μmol $[Ni(cod)_2]$; 25 μmol ligand; 1.25 mmol Lil; 2.5 mmol Et_3N ; 2 mL chlorobenzene; 2.5 mmol Zn; 72 h, 50 °C. [c] Determined by 1H NMR spectroscopy with an internal standard.

TONs can be achieved without the necessity to add Zn. It was shown earlier that ethene pressure has a beneficial effect on the replacement of acrylate from the nickel. Interestingly, under these conditions, even with the more stable 1,2-bis(diphenylphosphino)ethane (DPPE) as ligand TONs of 8 were measured (Table 3, entry 15). The TON was further increased to 21 with DCPP as ligand by decreasing the catalyst concentration in the presence of Zn (Table 3, entry 13). These results represent the first reported real catalytic formation of acrylate from ethene and CO_2 via an easy to manipulate process with cheap, commercially available reagents.

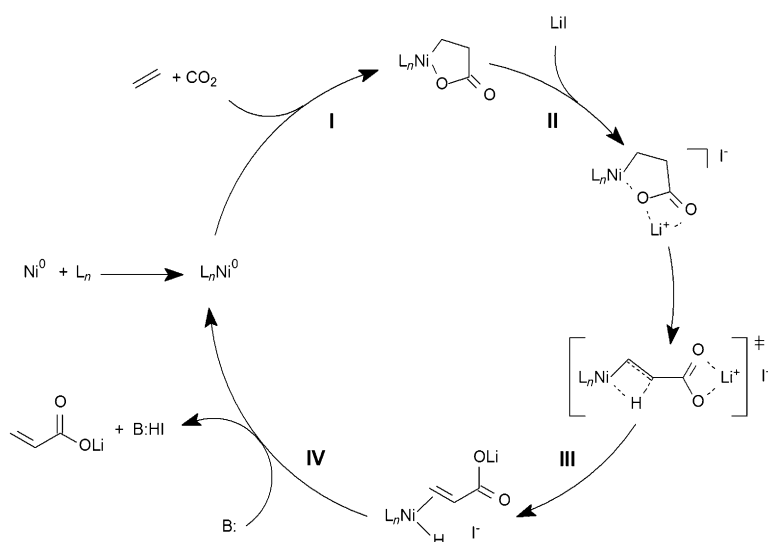
Based on literature reports and our own findings, a proposed catalytic cycle is depicted in Scheme 1.

In this report we presented a strikingly simple concept and results for the Ni-catalyzed conversion of ethene and CO_2 to acrylate with TONs of up to 21. This represents a major breakthrough for this “dream-reaction”. Although there is certainly a long way to go for any commercial application, these results provide a solid platform for further investigations to improve TONs and to convert also other alkenes to α,β -unsaturated carboxylic acids.

Experimental Section

All reactions were conducted in oven- or heat gun-dried glassware under an inert atmosphere of argon.

General procedure: To an oven-dried 4 mL vial with Lil (1.25 mmol) (and if applicable Zn-dust (2.5 mmol)) and equipped



Scheme 1. Proposed catalytic cycle for the Ni-catalyzed acrylate formation. The first step (I) involves the oxidative coupling of ethene and CO₂ on a Ni⁰ phosphine complex. This is followed by the coordination of the Lewis acid (Li⁺) to the carboxylate moiety of the lactone ring to facilitate Ni–O bond dissociation (II). Upon (partial) dissociation, β-H elimination can occur (III) with subsequent release of lithium acrylate and regeneration of the active Ni⁰ species by the base (IV).

with a magnetic stirrer bar, a solution of [Ni(cod)₂] (0.05 mmol) and ligand (0.05 mmol) in PhCl (2 mL) was added. The vial was closed with a screw cap with a PTFE/silicon septum, and to each vial Et₃N (2.5 mmol) was added via syringe. The vials were transferred to a 75 mL stainless steel autoclave and the septum punctured with a small needle. The autoclave was closed and pressurized to the required ethene pressure. After stirring for 2.5 h at room temperature, the autoclave was pressurized with additional CO₂ to the required pressure. The autoclave was heated to 50 °C for 72 h. After cooling to ambient temperature, the pressure was gradually released from the autoclave. The vials were removed from the autoclave and to each vial, 1000 μL D₂O with 0.25 mmol LiOAc·2H₂O was added as internal standard. After vigorous stirring for 30 min, the combined phases were filtered over cotton wool and the D₂O layer was separated from the organic phase. The turn over number was determined by ¹H NMR spectroscopy of the D₂O layer.

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Keywords: acrylates · carbon dioxide · homogeneous catalysis · Lewis acids · lithium · sustainable chemistry

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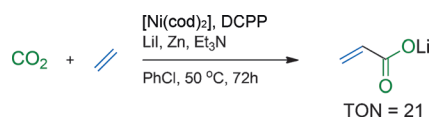
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COMMUNICATION

A dream comes true: CO₂ valorization by the catalytic formation of acrylates from carbon dioxide and ethene has been a significant challenge for several decades. Here a convenient method is presented for the catalytic formation of lithium acrylate from carbon dioxide and ethene in the presence of a strong Lewis acid with turnover numbers up to 21. DCPD = 1,3-bis(dicyclohexylphosphino)propane.

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