DOI: 10.1002/ange.201304529

CO_2 Utilization

Carbon Dioxide as a C_1 Building Block for the Formation of Carboxylic Acids by Formal Catalytic Hydrocarboxylation**

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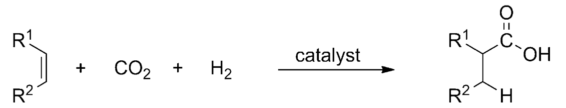
Carbon dioxide is an attractive carbon resource for exploitation in chemical transformations.[1] In particular, its use as C_1 building block in carbon–carbon bond-forming reactions would open new routes for the direct synthesis of carboxylic acids and their derivatives. However, the chemical inertness caused by the thermodynamic and kinetic stability of the CO_2 molecule pose major challenges for selective carbon dioxide transformation. Whereas there are well-established synthetic protocols for stoichiometric reactions with Grignard and other organometallic reagents, the direct catalytic synthesis of carboxylic acids from CO_2 and readily available substrates remains currently largely elusive.

Arene carboxylic acids can be prepared catalytically via their salts from substrates comprising C–Zn,[2] C–B,[3] or even C–Br[4] bonds. Arene C–H bonds were reported to be carboxylated by the use of substoichiometric amounts of Al_2Cl_6/Al.[5] Most recently, the catalytic carboxylation of C–H-acidic molecules was described for heterocycles,[6] polyhalogenated arenes,[6] and terminal alkynes.[7] The synthesis of acrylic acid from ethene and CO_2 in a stepwise manner was described;[8] this approach enabled repeated use of the Ni reagent corresponding to approximately 10 turnovers.[9] Furthermore, some examples were reported in which coupling reactions between CO_2 and alkenes,[10] dienes,[11] allenes,[12] or alkynes[13] in the presence of Pd, Ni, or Fe catalysts and superstoichiometric amounts of organometallic reducing agents, such as ZnR_2, AlR_3, Grignard reagents, and silanes, gave carboxylic acids after aqueous work up. Most notably, as early as 1978, the formation of propionic acid (38 % yield) from ethene and CO_2 was reported to occur under very drastic conditions ($p = 700$ bar, $T = 180\,°C$) in the presence of $[RhCl(PPh_3)_3]$ and HBr,[14] but details of this transformation remain unknown.

Herein we disclose a catalytic protocol for the synthesis of free carboxylic acids directly from CO_2, H_2, and simple olefins (Scheme 1). This transformation—formally referred to as hydrocarboxylation[15]—is thermodynamically feasible and provides an attractive direct route to free carboxylic acids through the use of CO_2 as a C_1 building block.



Scheme 1. Catalytic hydrocarboxylation of olefins with CO_2.

Our study was inspired by a transformation described by Simonato et al., who used formic acid as a hydrocarboxylation reagent.[16] As HCOOH is well-known to be accessible by the catalytic hydrogenation of carbon dioxide,[17] we envisaged the possibility of directly converting H_2, CO_2, and olefins into carboxylic acids. Cyclohexene (**1**) was used as the substrate for an initial screening of various metal complexes for the production of cyclohexanecarboxylic acid (**2**) or the undesired hydrogenation product cyclohexane (**3**) as two possible products. From a range of metal precursors and complexes, a combination of $[\{RhCl(CO)_2\}_2]$ and PPh_3 proved to be the most efficient catalyst system for the formation of **2** when CH_3I was added as a promoter. Hydrocarboxylation occurred selectively to give **2** in 69 % yield at 96 % conversion[18] along with the hydrogenation product **3** in 10 % yield and a trace amount of cyclohexyl iodide (**4**) as a by-product (Table 1, entry 2).

Significant further enhancement of the transformation towards the desired carboxylic acid product was observed when acidic additives were added to the reaction mixture. The most pronounced effect was observed with p-$TsOH{\cdot}H_2O$, in which case an additive/Rh ratio of 4:1 led to an 88 % yield of **2**, as determined by GC analysis. After aqueous workup, **2** was isolated in 86 % yield as a yellowish oil with higher than 97 % purity. Further purification by crystallization from pentane gave colorless crystals (see the Supporting Information for details). Optimization of the amount of the additive led to a remarkable maximum yield of **2** of 92 % at a 7:1 ratio of p-$TsOH{\cdot}H_2O$ to rhodium (Table 1, entry 8). The reaction could be carried out even in neat cyclohexene to avoid the use of acetic acid as a solvent, although under these conditions the

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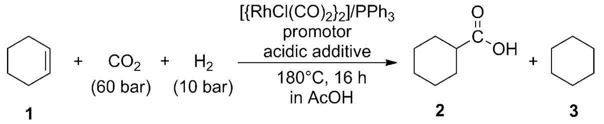
[**] This research was supported by a Kekulé grant (FCI) to T.G.O and the DFG (IRTG 1628 "SeleCa"). Additional support was received from the Cluster of Excellence "Tailor-Made Fuels from Biomass" (TMFB), which is funded by the Excellence Initiative of the German federal and state governments to promote science and research at German universities. We thank C. Merkens for collecting and Dr. M. Hölscher for solving the X-ray crystallographic data of $[Ph_3MePI][Rh(CO)(PPh_3)I_3]$ as well as C. Poßberg for HRMS measurements. Fruitful discussion with Prof. Dr. Willi Keim is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304529.

Table 1: Influence of different promotor compounds and acidic additives on the hydrocarboxylation of cyclohexene with CO_2 and H_2.[a]



1 **2** **3**

Entry	Promotor	Acidic additive[b]	Conv.[c] [%]	Yield of **2** [%][c]	Yield of **3** [%][c]
1	–	–	20	<1	5
2	CH_3I	–	96	69	10
3	CH_3I	HBTA	97	77	6
4	CH_3I	TFA	85	41	21
5	CH_3I	MSA	96	65	8
6	CH_3I	*p*-TsOH	99	75	4
7	CH_3I	*p*-TsOH·H_2O	99	88	2
8	CH_3I	*p*-TsOH·H_2O[d]	99	92	5
9	I_2	*p*-TsOH·H_2O	87	47	9
10	LiI	*p*-TsOH·H_2O	90	46	15
11	**4**	*p*-TsOH·H_2O	98	73	<1
12	**4** + LiI[e]	*p*-TsOH·H_2O	95	71	11

[a] Reactions were carried out with **1** (1.88 mmol), $[\{RhCl(CO)_2\}_2]$ (46 μmol), the promotor (925 μmol), Ph_3P (460 μmol), and the acidic additive (330 μmol) in acetic acid (0.65 mL) in a 10 mL autoclave (see the Supporting Information for details). [b] HBTA: bis(trifluoromethane)sulfonimide; TFA: trifluoroacetic acid; MSA: methanesulfonic acid; *p*-TsOH: *para*-toluenesulfonic acid. [c] Yields and conversion were determined by GC analysis. [d] The reaction was carried out with TsOH·H_2O (650 μmol). [e] The reaction was carried out with a **4**/LiI ratio of 2:8.

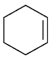
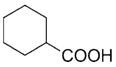
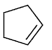
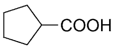
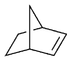
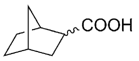
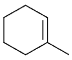
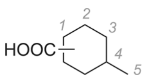
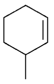
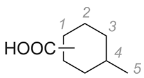
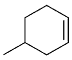
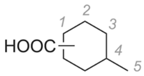
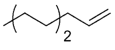
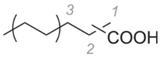
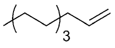
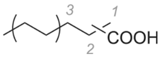
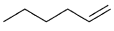
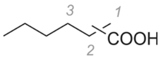
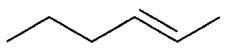
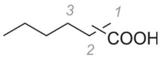
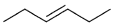
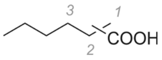
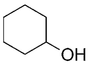
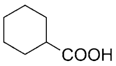
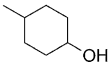
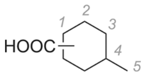
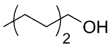
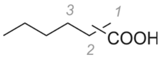
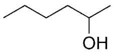
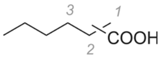
yield of **2** decreased to 59%. Notably, the optimized conditions rule out the formation of free formic acid as the actual reactant owing to the unfavorable thermodynamics of the formation of HCOOH from H_2 and CO_2 under acidic conditions.

In attempts to replace methyl iodide as the promotor, lithium iodide and I_2 also promoted reasonable conversion into **2** with yields around 47%, but their use resulted in a higher degree of hydrogenation to **3** (Table 1, entries 9 and 10). The application of other iodide salts, such as NaI and KI, proved inefficient and caused a drop in the yield of **2** below 10%.

Variation of the steric and electronic parameters of the phopshine showed that monodentate phosphines were generally suitable as ligands, whereas bi- and tridenate ligands led to complete suppression of the formation of **2**. A maximum yield of **2** was observed with a P/Rh ratio in the range of 5:1 to 8:1 with PPh_3, with rapid decay to values below 5% above and below these limits (see the Supporting Information for details).

Having established a standard set of reaction conditions, we surveyed the scope of the reaction (Table 2). With the substrate cyclopentene, a very good yield of 91% was observed for the desired hydrocarboxylation product (Table 2, entry 2; pentanecarboxylic acid was isolated in 82% yield). Norbornene was hydrocarboxylated in 62% yield with high *exo* selectivity (Table 2, entry 3). In the case of cyclohexenes with methyl substituents at different positions, isomeric mixtures of the carboxylation products were obtained in high yields, whereby the distribution of product

Table 2: Investigation of the scope of the hydrocarboxylation with CO_2 and H_2.[a]

Entry	Substrate	Product	Yield [%][b]	Conv. [%][b]
1			88 (86)	98
2			91 (81)	95
3[c]			*exo*: 50 *endo*: 12	93
4			73[d]	98
5			74[e]	97
6			77[f] (75)	99
7			74[g]	99
8			54[h]	>99
9			90[i] (76)	93
10			78[j]	97
11			78[k]	93
12			74 (73)	>99
13			74[l]	99
14			62[m] (55)	>99
15			64[n]	>99

[a] Reactions were carried out with the substrate (1.88 mmol), $[\{RhCl(CO)_2\}_2]$ (46 μmol), Ph_3P (460 μmol), *p*-TsOH·H_2O (330 μmol), and CH_3I (925 μmol) in acetic acid (0.65 mL) in a 10 mL autoclave. [b] Yields and conversion were determined by GC analysis. Yields in parentheses are for the isolated product. Workup procedures are provided in the Supporting Information. [c] The *exo*/*endo* selectivity was determined on the basis of ^1H NMR spectroscopy. [d] 1-CO_2H: 44%, 2/3-CO_2H: 20%, 5-CO_2H: 9%. [e] 1-CO_2H: 46%, 2/3-CO_2H: 20%, 5-CO_2H: 8%. [f] 1-CO_2H: 52%, 2/3-CO_2H: 18%, 5-CO_2H: 7%. [g] 1-CO_2H: 42%, 2-CO_2H: 22%, 3-CO_2H: 10%. [h] 1-CO_2H: 31%, 2-CO_2H: 17%, 3-CO_2H: 6%. [i] 1-CO_2H: 53%, 2-CO_2H: 26%, 3-CO_2H: 11%. [j] 1-CO_2H: 43%, 2-CO_2H: 24%, 3-CO_2H: 11%. [k] 1-CO_2H: 45%, 2-CO_2H: 23%, 3-CO_2H: 10%. [l] 1-CO_2H: 48%, 2/3-CO_2H: 19%, 5-CO_2H: 7%. [m] 1-CO_2H: 41%, 2-CO_2H: 15%, 3-CO_2H: 6%. [n] 1-CO_2H: 37%, 2-CO_2H: 19%, 3-CO_2H: 8%.

isomers was largely independent of the original substitution pattern (Table 2, entries 4–6). Similar observations were made for the hydrocarboxylation of linear *n*-alkenes bearing the double bond at the 1-, 2-, or 3-position (Table 2, entries 7–11). These product distributions are reminiscent of hydroformylation under isomerizing conditions[19] and indicate insertion into an rhodium–alkyl intermediate as a plausible step in the formation of the C–C bond.

The conversion/time profile for the conversion of cyclohexene (**1**) under standard conditions is depicted in Figure 1. Full conversion of **1** was observed after 16 h, at which time the main product cyclohexanecarboxylic acid (**2**) was present in 84 % yield. However, the formation of **2** started only after an induction period of about 1 h. During this period, the rapid formation of cyclohexyl iodide (**4**) was observed. The yield of **4** reached a maximum of about 16 % before this compound was consumed, and cyclohexyl acetate (**5**) and **2** were formed. At the highest rate of formation of the product **2**, the amount of **5** present in the solution reached a maximum of about 3 %. Cyclohexane (**3**) is only a minor by-product, the amount of which never exceeded 5 % during the course of the reaction.

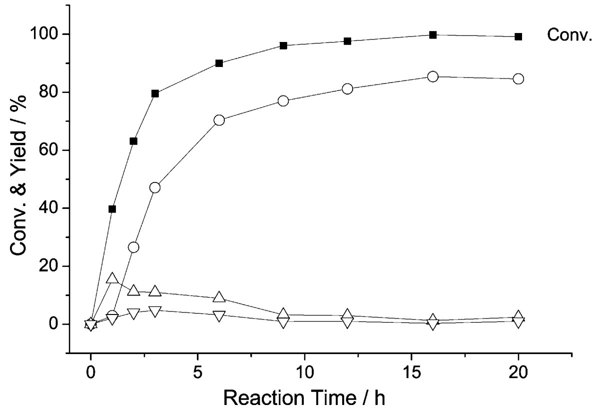
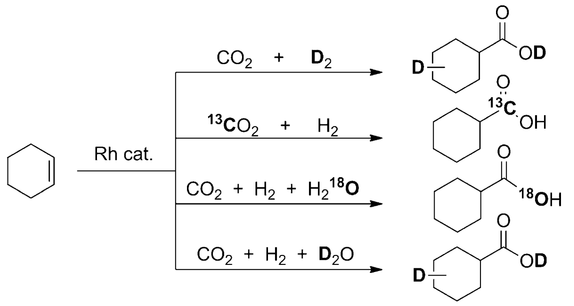


Figure 1. Conversion and yield of the major intermediates and products with respect to the reaction time for the hydrocarboxylation of cyclohexene (**1**) under standard conditions (see Table 1, entry 7): ○ **2**, △ **4**, ▽ **5**.

The observed conversion/time profile is most consistent with the initial formation of **4** from cyclohexene (**1**) in the presence of the iodide source. However, **4** does not appear to be the most reactive intermediate, but is converted by reaction with the solvent acetic acid into the acetate **5**, which is readily consumed in the catalytic transformation. Indeed, the use of **5** as the substrate also gave **2** in 71 % yield at 95 % conversion under the standard conditions. Consequently, alcohols can also be used efficiently as substrates: the conversion and product distribution were almost identical to those observed with comparably substituted alkenes (Table 2, entries 12–15). This extension to alcohol substrates widens the potential synthetic scope of the transformations significantly.

Intrigued by the observation of initially formed cyclohexyl iodide (**4**) in the conversion/time profile, we applied this compound instead of CH_3I as a promotor for the catalytic system. With a Rh/**4** ratio of 1:10, full conversion of cyclohexene (**1**) was reached to give **2** in 73 % yield if both **1** and **4** are considered as the alkyl source (Table 1, entry 11). An Rh/**4** ratio of 1:2 still resulted in a 54 % yield of **2**, and this yield could be increased to 71 % by the addition of LiI (Table 1, entry 12).

Insight into the reaction mechanism was obtained from isotope-labeling studies (Scheme 2). The use of D_2 instead of hydrogen resulted in deuterium incorporation with a large degree of scrambling around the cyclohexyl ring. Similar isotopic patterns were observed when D_2O was added to the reaction mixture. The use of a $^{13}CO_2$-enriched gas mixture proved unambiguously that CO_2 was the source of carbon in the carboxylic acid functionality by a corresponding increase in the ^{13}C NMR signal. Most significantly, however, incorporation of ^{18}O in the carboxylic acid moiety was observed by mass spectrometry when the reaction was carried out in the presence of $H_2{}^{18}O$. No ^{18}O was incorporated in the carboxylic acid group when **2** was exposed to $H_2{}^{18}O$ under the reaction conditions in control experiments. This result clearly indicates that the carboxylic acid group is not constructed by the incorporation of an intact CO_2 molecule, but rather suggests a hydroxycarbonylation pathway involving carbon monoxide (CO) and water as reactive species.



Scheme 2. Isotopic labeling pattern observed by NMR spectroscopy and MS for the rhodium-catalyzed reaction of cyclohexene (**1**) with CO_2 and H_2 under the standard conditions (see Table 2). $H_2{}^{18}O/D_2O$ (16.7 mmol) was added in addition to the standard reagents in the experiments with labeled water (see the Supporting Information for details).

The formation of CO under the reaction conditions by a reverse water–gas shift reaction (rWGSR) was corroborated by GC analysis of the gas phase with $[\{RhCl(CO)_2\}_2]$ or RhI_3 as the catalyst precursor in the absence of cyclohexene (see the Supporting Information for details). Control experiments in which CO (5 bar) and H_2 gas (10 bar) were used under the standard conditions with p-TsOH·H_2O as a water source gave **2** in 79 % yield. An increase in the partial pressure of CO above 30 bar, however, resulted in a sharp decrease in the yield of **2**, which indicated catalyst poisoning.

The importance of the coordination ability of CO, PPh_3, and I^- at rhodium as the catalytically active center is illustrated by the isolation of an unprecedented monomeric anionic Rh^{III} complex containing all three components in its ligand sphere (Figure 2). When left to stand in air after complete conversion of the substrate, the red reaction solution turned dark brown within minutes, and brown crystals suitable for X-ray crystallographic analysis could be obtained by slow evaporation of the solvent. The molecular structure revealed a slightly distorted octahedral arrangement

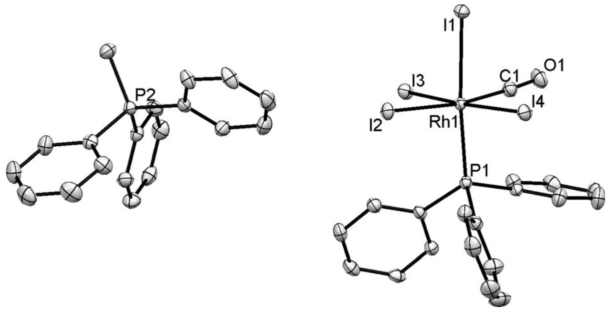
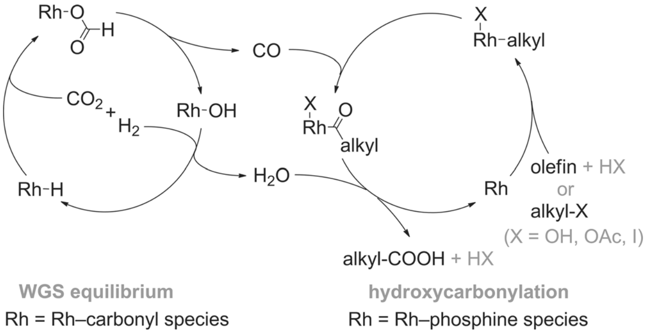


Figure 2. Molecular structure of $[CH_3PPh_3][RhI_4(CO)(PPh_3)]$ as determined by single-crystal X-ray diffraction. Hydrogen substituents are omitted for clarity. Thermal ellipsoids are at the 50% probability level. See the Supporting Information for structural parameters.

at the Rh^{III} center with four iodide ligands spanning two triangular faces and the PPh_3 and CO ligands arranged *cis* to one another at the remaining coordination sites. The phosphonium cation $[CH_3PPh_3]^+$, which acts as a counterion, is most likely formed by the reaction of PPh_3 with CH_3I.

In agreement with all experimental findings, a combination of two rhodium catalytic cycles is proposed to facilitate the synthesis of carboxylic acids from olefins or alcohols, CO_2, and H_2 in the present system (Scheme 3). In one cycle, the rhodium-catalyzed rWGSR sets up an equilibrium between CO_2/H_2 and CO/H_2O. In the second cycle, the substrates undergo hydroxycarbonylation through the reversible formation of a rhodium–alkyl intermediate. A combination of rWGSR and carbonylation was described earlier for ruthenium catalysts under basic conditions but resulted in reductive formation of the C_1-elongated alcohols.[20] The WGS equilibrium is typically adjusted under basic conditions; however, activity of Rh catalysts under acidic conditions has been noted previously.[21] Although the exact details of the two cycles remain the subject of further studies, these catalytic cycles bear resemblance to well-established rhodium and palladium catalysis in the Monsanto process,[22] hydroformylation,[19] and other carbonylation[23] processes. Hence, the rWGSR cycle would be expected to be favored by species with a lower P/Rh ratio, whereas the carbonylation cycle would benefit from PPh_3 in the coordination sphere. In good agreement with this hypothesis, almost no production of **2** was observed when PPh_3 was omitted from the optimized reaction conditions. Similarly, the positive effect of I^- and H^+ can be rationalized qualitatively by the need to balance the stabilization of the intermediates in a dynamic equilibrium between the two cycles.



Scheme 3. Proposed mechanism of the overall hydrocarboxylation as coupled catalytic cycles of the WGS equilibrium and hydroxycarbonylation.

In summary, an effective catalytic system was identified for the direct formation of carboxylic acids from non-activated olefins, CO_2, and H_2 with high conversion and selectivity under optimized reaction conditions. Internal and terminal olefins were converted with regioselectivities similar to those observed in hydroformylation. Other substrates that are able to form rhodium–alkyl intermediates under the reaction conditions may also undergo this transformation, as shown in particular for primary and secondary alcohols. Mechanistic studies suggest that the formal hydrocarboxylation results from a combination of rhodium-catalyzed rWGSR and hydroxycarbonylation cycles. Thus, the present findings provide a new approach for the catalytic synthesis of carboxylic acids by using CO_2 as a C_1 building block.

Experimental Section

General procedure: Under an argon atmosphere, $[\{RhCl(CO)_2\}_2]$ (46.0 μmol), an olefin (1.88 mmol), and CH_3I (925 μmol) were placed in a Schlenk tube along with acetic acid (0.65 mL). The red-brown solution was transferred with a cannula to a stainless-steel autoclave containing PPh_3 (460 μmol) and *p*-TsOH·H_2O (330 μmol). The autoclave was pressurized with CO_2 (4.1 g), and then H_2 (10 bar) was added to give a total pressure of about 70 bar at room temperature. The reaction mixture was stirred and heated to 180 °C in an aluminum cylinder. After 16 h, the autoclave was cooled to 0 °C and then carefully vented. The resulting mixture was analyzed by gas chromatography with 1-phenylethanol and *n*-dodecane as internal standards. Product yields (Y) were found to be reproducible within $\Delta Y = \pm 2\%$ in two independent reactions for selected experiments.

Received: May 26, 2013
Revised: July 29, 2013
Published online: September 3, 2013

Keywords: carbon dioxide · carboxylic acids · homogeneous catalysis · hydrocarboxylation · rhodium

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