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Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ISSN 1359-7345

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DOI: 10.1039/C8CC03157F

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COMMUNICATION

Transfer Hydrogenation of Carbon Dioxide and Bicarbonate from Glycerol Under Aqueous Conditions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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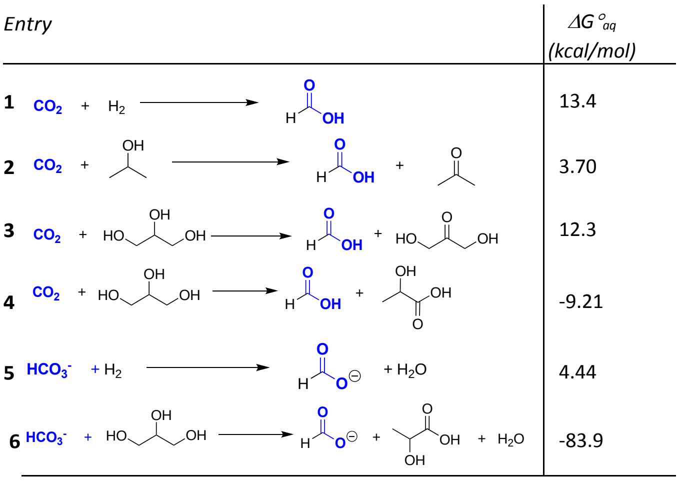
The transfer hydrogenation of CO_2 from glycerol to afford formic and lactic acid is a highly attractive path to valorizing two waste streams, and is significantly more thermodynamically favorable process than direct CO_2 hydrogenation. We report the first homogeneous catalyst for this transformation, consisting of water-soluble Ru N-heterocyclic carbene complex. The catalyst affords lactic and formic acid selectively in the presence of base at temperatures between 150 and 225 ˚C. Carbonate salts can also be utilized in place of CO_2, affording the same products at higher rates.

Methods to convert CO_2 to formaldehyde, formic acid (FA) and methanol have been the subject of intense investigation in recent years, given the abundance of CO_2 as a C1 feedstock.[1] Among these products, FA is particularly attractive due to its widespread utility as a chemical feedstock,[2] commodity chemical for food and agriculture,[2] fuel[3] and hydrogen storage medium.[4] Catalytic methods for CO_2 direct hydrogenation continue to be intensively studied: highly active homogeneous catalysts with Rh,[5] Ru,[6] Ir,[7] Fe[8] and Co[9] have been reported, with turnover numbers (TONs) on the order of 10^6. Base or amine additives help stabilize the product as formate, but recent examples demonstrate the feasibility of the aqueous reaction in the absence of additives.[6c, 10] Since CO_2 is in equilibrium with HCO_3^- in aqueous media ($pK_{a1} = 6.35$), hydrogenation of bicarbonate has also been demonstrated with Rh[5, 11], Ru[12], Ir[13] and Fe[14] catalysts. However, reported activities are often lower than those for CO_2, despite the fact that the thermodynamics of bicarbonate hydrogenation in water are reported to be slightly more favourable than that of CO_2.[15]

Although a number of highly active catalysts for direct hydrogenation of CO_2 have been reported, the ability to directly utilize a renewable source of hydrogen would be highly advantageous from a sustainability perspective. Transfer hydrogenation (TH) from a renewable hydrogen source could also afford an additional product in a single process. The generation of an additional by-product could improve the economics of the process, provided the product is more valuable than the hydrogen donor and is formed selectively, and could offer additional thermodynamic driving force for the reaction.

We thus compared free energies of reaction for direct hydrogenation and transfer hydrogenation of CO_2 in aqueous media. TH from isopropanol, a common H_2-donor, is more favourable by ca. 9.7 kcal/mol compared to direct hydrogenation of CO_2 (Scheme 1, entries 1-2). Catalytic examples of TH from isopropanol have been reported by Peris et al[1e] using water-soluble Ru and Ir NHC complexes.[16] Compared to isopropanol, glycerol is a more desirable H_2-donor due to its abundant supply as a renewable by-product of biodiesel production. Furthermore, using glycerol as hydrogen donor in TH of CO_2 could provide a route to glycerol valorization.[17] However, CO_2 TH from glycerol is considered challenging compared to reactions with isopropanol.[18]

Scheme 1. Calculated free energies of reaction ($\Delta G°_{aq}$) for the CO_2 direct hydrogenation and transfer hydrogenation (Gaussian16, G3B3, PCM water). [a] Reaction includes carbonate base, and was calculated as-stated.



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† Electronic Supplementary Information (ESI) available: (catalyst synthesis, characterization, and additional figures/tables). See DOI: 10.1039/x0xx00000x

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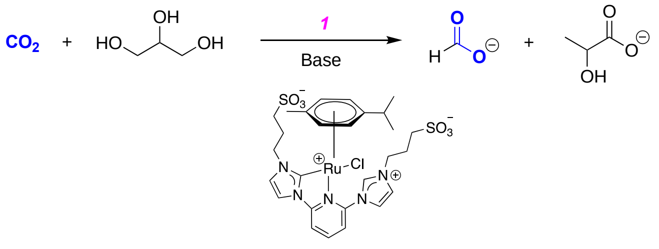
DOI: 10.1039/C8CC03157E

This notion is consistent with our calculations, which show $\Delta G°_{aq}$ of CO_2 TH from glycerol (entry 3) is 8.6 kcal/mol *less* favourable than TH from isopropanol when dihydroxyacetone (DHA) is the glycerol by-product. However, recent reports show that glycerol dehydrogenation reactions under basic conditions afford lactic acid,[19-20] likely via DHA isomerization, dehydration and intramolecular Cannizzaro reaction.[19a] When lactic acid is the glycerol by-product, CO_2 TH becomes 22.6 kcal/mol *more* favourable than direct hydrogenation (entries 4 and 1). Furthermore, while all CO_2 hydrogenation processes are more favourable in the presence of base, the formation of two acids in the reaction of CO_2 and glycerol provides additional driving force under basic conditions (ESI Table S2). Consistent with this, the calculated $\Delta G°_{aq}$ for TH of bicarbonate from glycerol is also highly favourable (entry 6).

Given that the TH from glycerol to CO_2 or bicarbonate is thermodynamically favourable, we were surprised that catalytic examples of this reaction have not been more extensively exploited. In the first of two important advances, Lin et al reported use of heterogeneous Pd/C for TH of bicarbonate using glycerol, but with CO_2 only 22 turnovers were obtained in 12 hours at 240 ºC.[18a] In a significant advance towards a homogeneous process, Aresta et al reported a stoichiometric reaction of $RuCl_2(PPh_3)_2$ with CO_2 in aqueous glycerol, which affords glycolic and formic acid at 82 ºC.[18b] The authors propose that DHA undergoes dehydrogenation and decarbonylation to afford glycolic acid and Ru(H)(CO)(formate), and the latter could not eliminate formic acid. This suggests that preventing decarbonylation is important for facilitating catalytic turnover.

Here were we report the first homogeneous catalyst with appreciable activity for the TH of glycerol with CO_2 and bicarbonate, selectively affording lactic and formic acids with high turnover numbers and concentrations that show potential for development into a competitive hydrogenation process.

Scheme 2



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Recently we reported that Ir and Ru *N*-heterocyclic carbene (NHC) complexes with sulfonate-functionalized wingtips are highly active for acceptorless dehydrogenation of glycerol to lactic acid,[20] with no detectable formation of decarbonylation product. When we performed this reaction with carbonate as base, formate was observed. This prompted us to examine a series of water-soluble complexes for TH of both bicarbonate and CO_2 from glycerol. This initial report focuses on the most active Ru compound we have identified, Ru(II) CNC with propanesulfonate wingtips (***1***), synthesized via a literature procedure.[21]

Transfer hydrogenation reactions were carried out in a high-pressure Parr reactor and sampled periodically, maintaining the designated CO_2 pressure. Products were identified and quantitated with HPLC (ESI Figure S1) and ^1H NMR (Figure 2) with an internal standard. Control reaction without catalyst afford no appreciable conversion of glycerol, while control reactions without CO_2 or carbonate afford only lactate. Esters of glycerol lactate or formate were not observed under basic conditions. An extensive series of optimization reactions was performed for this process, given that the speciation of CO_2 in aqueous solution is pH-dependent, and that catalyst ***1*** was suspected to be also capable of facilitating pH-dependent formate dehydrogenation.

Therefore, it was not surprising that the turnovers of lactate and formate observed with catalyst ***1*** were found to depend on the temperature and availability of base. In the absence of base, no products are observed from a reaction at 150 °C. However, reactions with cat ***1*** (0.15 mM), 1 M KOH, 1:1 glycerol:water (conditions optimized previously for glyceroat 46 bar CO_2 and 150 °C afford 330 turnovers in 24 h, equivalent to ~50 mM of formate and lactate (Table S1 entry 3). Further increase in reaction time afforded more lactic but no more formic acid. Doubling the base concentration (2 M KOH) affords similar TONs in 24 hours, but the initial activity (TON at t=1hr) is doubled (Table S1 entry 4). This is attributed to the fact that the initial KOH concentration is higher for the reaction with 2 M KOH, resulting in higher initial rate. However, as the vessel is pressurized, the KOH solubility reaches saturation, which results in a similar effective base concentration in both reactions. When KOH concentration is decreased to 0.25 M, the reaction still affords ~50 mM lactate, but significantly less formate (18 mM, Table S1 entry 1), and a drop in pH to 6.9 is observed after 24 hr. The 1-hr TONs are 141 and 71 respectively for lactate and formate, with lactate concentration steadily increasing and that of formate becoming steady (ESI Figure S2-a). We hypothesized this observation was due to competing CO_2 hydrogenation and formic acid dehydrogenation at the lower pH. Indeed, experiments with cat ***1*** at 150 °C confirm that the catalyst has pH-dependent activity for decomposition of formic acid/formate (Figure S4).

Given that maintaining high pH is necessary to minimize formate decomposition, we opted to increase the effective base concentration by decreasing CO_2 pressure. A reaction with 26 bar CO_2 at 150 °C and 2 M KOH affords almost double the activity observed with 48 bar CO_2 (~600 turnovers in 24 hr, Figure 1a and Table S1 entry 7). Thus, lower CO_2 pressure is favourable for both formate and lactate production. When the same reaction was performed at 180 °C, the catalyst affords 1065 turnovers of formate and 1685 of lactate in 24 hr (Figures 1b), corresponding to 166 mM and 262 mM respectively. The reaction was monitored until 86 hr, at which time TONs of lactate and formate reached 5046 and 2200 respectively (NMR spectra in Figure 2). The difference in formate vs lactate concentration is likely the result of catalytic dehydrogenation and thermal decomoposition of potassium formate (thermally decomposes at 167 °C[22]).

Further increase in reaction temperature exacerbates the difference in lactate vs formate produced. In addition, at temperatures higher than 180 °C significant etching is observed on the glass insert of the autoclave, which necessitates the use of lower base concentration. For example, at 225 °C the reaction could only be performed with 0.25 M KOH, affording 0.328 M lactate (3160 turnovers), but only 28 mM formate (268 turnovers) in 24 hours (ESI Figure S2).

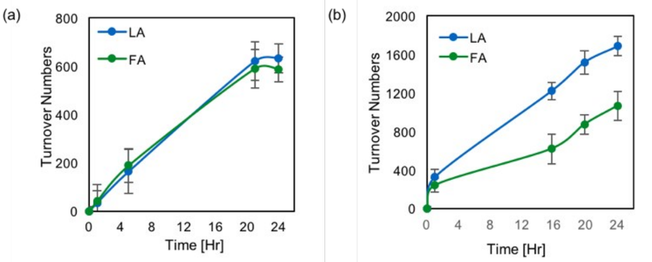


Figure 1. Time course for production of formate and lactate from the reaction of CO_2 and glycerol using catalyst ***1*** using pCO_2 26 Bar, 6.85 M aqueous glycerol and 2.00 M KOH at (a) 150 °C and (b) 180 °C. Error bars based on average of two replicates.

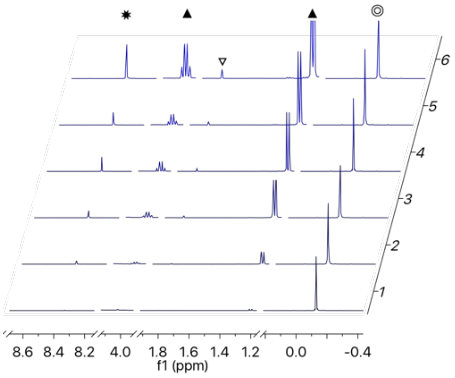


Figure 2. Sections of ^1H NMR spectra corresponding to t=0 (*1*), t=1h (*2*), t=8h; t=15h (3), t=19h (*4*), t=24h (*5*) and t=86 h (6) for reaction of CO_2 and glycerol using catalyst ***1*** *(*pCO2 26 Bar, 6.85 M aqueous glycerol and 2.00 M KOH at 180 °C). Key: ▲ Lactate; ✷ Formate; ▽Pyruvaldehyde; ◎TSP (standard).

The effect of temperature, base and CO_2 pressure are summarized by contour plots based on temperature and the "effective" base concentration (estimated as $[KOH]/p(CO_2)$) (Figure 3). Thus, optimal equimolar production of formate and lactate occurs when temperature and effective base concentration are maximized. However, higher lactate production can be achieved with higher reaction temperature and lower base concentration. The conditions can thus be used to "tune" the ratio of formate and lactate produced.

Given that CO_2 in aqueous base forms carbonate and bicarbonate, we performed a reaction with 2.0 M K_2CO_3 and 26 bar N_2 at 150 °C. Carbonate was selected over bicarbonate in order to increase initial pH. The initial pH of 12.1 drops to 10.8 over 20 hours of reaction. The theoretical ratios of HCO_3^-:CO_3^{2-} at pH 12.1 and 10.8 are 2:98 and 40:60 respectively, which is important because bicarbonate is likely the only species that can undergo transfer hydrogenation.[15] In 20 hours the reaction affords 42610, 3588 and 5649 turnovers respectively of lactate, formate and 1,2-PDO (Figure 4 and additional visualization in Figure S4). The formate yield based on carbonate is 25% (505 mM formate). The higher lactate vs formate concentration observed is consistent with previous observations of dehydrogenation activity of cat ***1*** at lower pH (Figure S4). PDO is only observed under the lower pH conditions, as we previously reported.[21]

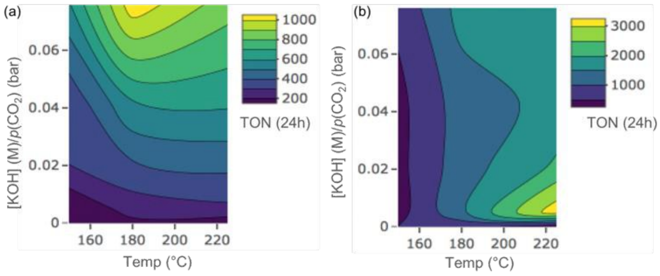


Figure 3. Contour plots showing TONs in 24h for (a) formate and (b) lactate using cat ***1***.

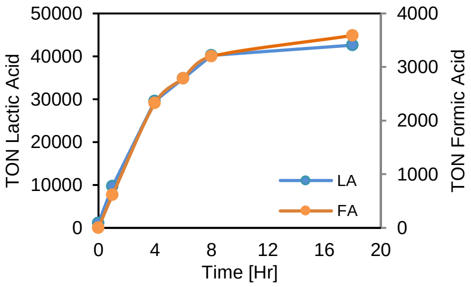
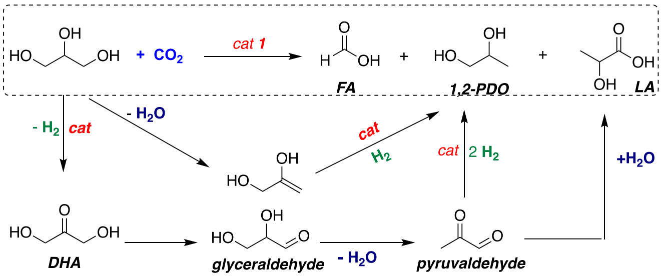


Figure 4. Time course for production of formate and lactate from the reaction of glycerol using catalyst ***1*** using pN_2 26 Bar, 6.85 M aqueous glycerol, 2.00 M K_2CO_3, at 150 °C.

We propose a mechanism for PDO formation either via (i) dehydration, transfer hydrogenation, or (ii) dehydrogenation to DHA or glyceraldehyde, then dehydration and transfer hydrogenation. The only proposed intermediate that has been directly observed is minute amounts of pyruvaldehyde (Figure 2).

Scheme 3. Proposed route to lactic acid and 1,2-PDO from glycerol transfer hydrogenation.



We considered potential formation of lactate and formate esters as side reactions that could interfere with product quantitation. Thus, formate and lactate esters of glycerol were synthesized under acidic conditions and characterized by NMR (ESI Figure S5). These esters were not observed by NMR in the reactions under the current conditions.

Mechanistically, we postulate that the TH likely proceeds via coordination of glycerol, followed by deprotonation by base. Subsequent β-hydride elimination likely occurs at the secondary position of glycerol, affording Ru-H and DHA. DHA is converted

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to lactic acid via isomerization, dehydration and intramolecular Cannizzaro reaction.[19b] Bicarbonate next binds to the catalyst and undergoes a hydroxide elimination, which has been previously proposed by DFT calculations for the Ru-catalysed hydrogenation of bicarbonate.[15] The resulting H-Ru-CO_2 complex undergoes insertion[15, 23] to generate ruthenium formate. The final formate dissociation is likely facilitated by the polar aqueous reaction medium, which allows excellent solvation of formate anions, making the dissociation energetically possible in water. [15]

Conclusions

Here we demonstrate a homogeneous catalytic process for CO_2 and bicarbonate transfer hydrogenation (TH) from glycerol with a water-soluble Ru *N*-heterocyclic carbene complex (cat ***1***) and base. The reaction selectively affords two value-added products: potassium formate and lactate. Calculations show that TH of CO_2 and bicarbonate are made thermodynamically more favourable by the ultimate conversion of glycerol to lactic acid. As a result, CO_2 TH from glycerol becomes significantly more favorable than direct hydrogenation under basic conditions. Equimolar amounts of lactate and formate are afforded (~600 turnovers) at 150 ˚C, while greater lactate than formate production is observed at T > 150 ˚C. At 180 ˚C cat ***1*** affords 1685 and 1065 turnovers respectively of lactate and formate in 24 h. Carbonate salts can also be utilized in place of CO_2, affording 42610, 3588 and 5649 turnovers respectively for lactate, formate and 1,2-propanediol. A preliminary mechanism is proposed, but further experimental and theoretical investigations of mechanism, as well as comparable activity of other catalyst precursors, are under investigation.

Conflicts of interest

There are no conflicts to declare.

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