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Homogeneous Hydrogenation of CO_2 to Methyl Formate Utilizing Switchable Ionic Liquids

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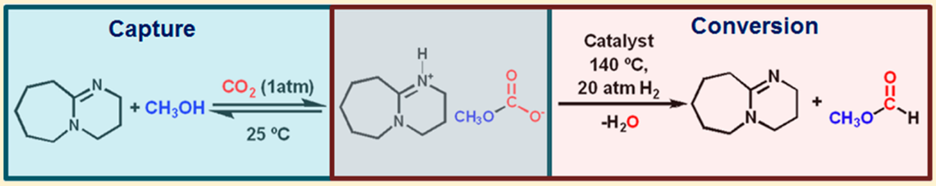
Supporting Information



ABSTRACT: Combined capture of CO_2 and subsequent hydrogenation allows for base/methanol-promoted homogeneous hydrogenation of CO_2 to methyl formate. The CO_2, captured as an amidinium methyl carbonate, reacts with H_2 with no applied pressure of CO_2 in the presence of a catalyst to produce sequentially amidinium formate, then methyl formate. The production of methyl formate releases the base back into the system, thereby reducing one of the flaws of catalytic hydrogenations of CO_2: the notable consumption of one mole of base per mole of formate produced. The reaction proceeds under 20 atm of H_2 with selectivity to formate favored by the presence of excess base and lower temperatures (110 °C), while excess alcohol and higher temperatures (140 °C) favor methyl formate. Known CO_2 hydrogenation catalysts are active in the ionic liquid medium with turnover numbers as high as 5000. It is unclear as to whether the alkyl carbonate or CO_2 is hydrogenated, as we show they are in equilibrium in this system. The availability of both CO_2 and the alkyl carbonate as reactive species may result in new catalyst designs and free energy pathways for CO_2 that may entail different selectivity or kinetic activity.

INTRODUCTION

Carbon dioxide has been widely recognized as a potent greenhouse gas and is linked to global warming.[1−3] As a result, recycling of CO_2 has been a topic of intense research[4−11] and a subject of discussion not only from a scientific but also from an ecological−political point of view. Because CO_2 is a highly oxidized, thermodynamically stable compound, its utilization requires reaction with high-energy substances. Also, while CO_2 may be abundant, its separation, purification, and compression are energy-intensive processes. Combining the chemical capture and conversion of CO_2 into useful products into one step removes large inefficiencies of separate capture and conversion, but also entails potentially new reactivity that may enable faster and more economical catalytic conversions of CO_2. Catalytic hydrogenation is one approach to CO_2 fixation. Hydrogenation of CO_2 can lead to a variety of useful compounds such as methanol, hydrocarbons, esters, and ethers.[12] Of these, methanol holds a central position, as it is a key petrochemical.[13] One path for the homogeneously catalyzed hydrogenation of CO_2 to methanol begins with hydrogenation of CO_2 into formate, which has been studied by several research groups.[14−17] Researchers have developed catalysts from precious metals[14−27] and nonprecious metals[28−31] utilizing supercritical fluids,[32] water,[33] or ionic liquids[34] with varying degrees of success. The second step toward methanol involves esterification reactions of the formate with an alcohol, which has been demonstrated by direct hydrogenation of CO_2 in the presence of alcohols.[14−17] Lastly, hydrogenations of formate esters have been demonstrated by Milstein, Sanford, and Leitner to yield methanol.[14−17,35] Nearly all reactions currently require moderate to high pressures of CO_2.

There are two primary methods employed to make the hydrogenation of CO_2 into formic acid more favorable: trapping formic acid as formate salts and using highly polar solvents. As CO_2 hydrogenations to produce formic acid are endergonic, the easiest method to force the reaction to become exergonic is to add base to produce formate salts.[24] Solvent stabilization has also been shown to promote the hydrogenation of CO_2, where more polar solvents such as water or ionic liquids stabilize formic acid and formate salts.[34] The degree of stabilization of formic acid and formate salts follows the trend of ionic liquid > water > alcohols, ethers.

Since catalytic hydrogenations of CO_2 to formate salts can be made favorable with bases and highly polar media, combining the bases and the polar media such as in a switchable ionic liquid may lead to further rate enhancements. Switchable ionic liquids (SWILs) are materials that convert from a molecular relatively nonpolar liquid to a highly polar ionic liquid by the reversible complexation with CO_2.[36] SWILs are blends of alcohols and amidine or guanidine bases that chemically react with or capture CO_2 to form amidinium or guanidium alkyl carbonate ionic liquids at low or moderate pressures.[36] These ionic liquids can contain 15 wt % (1:1 mol %) CO_2 chemically fixated in solution at room temperature and 1 atm. In addition,

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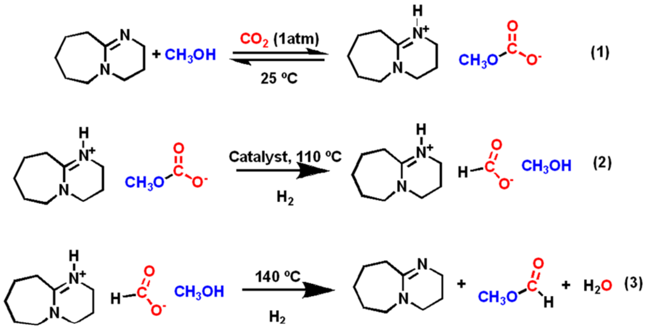
SWILs can also physically dissolve additional CO_2 under pressure.[37] The available concentration of CO_2 in solution is far greater than other conventional solvents or traditional ionic liquids at ambient pressure, thus opening new possibilities for catalytic hydrogenations at lower pressures. This paper investigates the hydrogenation of the "captured" CO_2 to formate and subsequent esterification of formate to methyl formate under atmospheric pressure of CO_2.

RESULTS AND DISCUSSION

Scheme 1 outlines a proposed hydrogenation pathway of CO_2 to methyl formate in three distinct steps. Step 1 is the capture and possible "activation" of CO_2 by DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and an alcohol to form the alkyl carbonate ionic liquid. Step 2 is the hydrogenation of the alkyl carbonate into the [$DBUH^+$] formate. The third step is esterification of [$DBUH^+$] formate with the previously liberated alcohol from step 2, making an alkyl formate, liberating base and water.

Scheme 1. Proposed Preparation of Methyl Formate from CO_2 and H_2 in DBU−Methanol-Based Switchable Ionic Liquid



To investigate the possibility of this CO_2 reduction scheme, we studied each step along the path. We have previously shown that methyl carbonate [$DBUH^+$] salts can be formed in close to quantitative yields at 1 atm, step 1 of Scheme 1.[38] Hydrogenations of [$DBUH^+$] methyl carbonate, [$DBUH^+$] propyl carbonate, and [$DBUH^+$] hexyl carbonate using ruthenium-based catalysts known for their ability to hydrogenate CO_2 were investigated as representative systems for step 2. The hydrogenation of [$DBUH^+$] methyl carbonate to [$DBUH^+$] formate (Figure 1) was found to proceed in appreciable conversion with selectivity for [$DBUH^+$] formate salt. The hydrogenation reactions were performed at 110 °C, 20 atm of H_2, for 16 h, with the only CO_2 in the system provided by [$DBUH^+$] methyl carbonate.

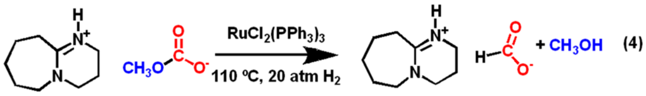


Figure 1. Hydrogenation of [$DBUH^+$] methyl carbonate to [$DBUH^+$] formate.

The $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture after 16 h, collected at 110 °C (Table 1, entry 1), is shown in Figure S1. The peak at 162.8 ppm corresponds to the protonated amidinium carbon in [$DBUH^+$], while the peak at 166.9 ppm corresponds to the formate product and the peak at 158.4 ppm corresponds to the carbonyl carbon of the methyl carbonate anion. A proton-coupled ^{13}C NMR spectrum (Figure S1, inset) shows the formate carbon split into its expected doublet with a $^1J(C-H)$ of 180 Hz.[18]

Crystallographic analysis of the isolated crystals from the reaction solution confirmed the [$DBUH^+$] formate structure (see the Supporting Information, Figure S2).

Step 3 in Scheme 1 was found to proceed under the same conditions of step 2, albeit at increased temperatures (Figure 2). The results of the experiments are tabulated in Table 1. Performing reaction 1 at 110 °C immediately followed by heating of the reaction product mixtures to 140 °C for 40 h was found to convert methyl carbonate to methyl formate. Alternatively, a direct hydrogenation of methyl carbonate to methyl formate was performed using the same conditions of step 2 but heated to 140 °C for 40 h instead of 110 °C at 16 h. The esterification reaction between the produced [$DBUH^+$] formate and methanol (the C−O bond cleavage) may be rate limiting.[19] In the absence of the metal catalyst no esterification of [$DBUH^+$] formate (independently synthesized) was observed under the reaction conditions used in this study, suggesting the metal catalyst is necessary for esterification.

We found that ruthenium- and iron-based catalysts were active, with best activities for ruthenium-based catalysts. The two heterogeneous catalysts tested showed no hydrogenation activity under the reaction conditions employed, Table S1.

We performed multiple hydrogenation experiments for reaction 4 using [$DBUH^+$] methyl carbonate with homogeneous catalysts known to hydrogenate CO_2 (Table 1). Additionally, the system was run in SWILs with different alcohol chain lengths (Table 2), at different catalyst loadings (Table 3), and with varied CO_2 pressures (Table 4). The hexyl carbonate was found to be least active; the propyl carbonate was intermediate in activity, while the methyl carbonate was found to be most active. We believe this is due to the higher polarity of the methyl carbonate compared to the hexyl carbonate. We have previously shown that the degree of ionic conversion (alkyl carbonate concentration) in switchable ionic liquids is sensitive to polarity,[39,40] and we hypothesize that the free energy of step 2 can be impacted by the inherent polarity of the ionic liquid. Thus, the more polar methyl carbonate will allow stronger solvent stabilization of the produced formate salts compared to the less polar hexyl carbonate.[38,41] The best TON (5100) was achieved using $RuCl_2(PPh_3)_3$ at substrate-to-catalyst loadings of 8650.

Hydrolysis of DBU into a cyclic lactam (Figure 2, confirmed by $^{13}C\{^1H\}$ NMR) is caused by the water released during esterficiation. This hydrolysis appears to be quantitative based upon the water released. This hydrolysis lactam of DBU is similar to the lactam of hydrolyzed 1,5-diazabiciclo-[3.4.0]non-5-ene (DBN), which had been previously synthesized and characterized by Pereira et al.[42] Experiments without a metal catalyst at 140 °C with [$DBUH^+$] methyl carbonate in methanol showed negligible hydrolysis (Figure S3); therefore it is surmised that the hydrolysis was occurring from water produced during the catalyzed reaction. Attempts to use drying agents such as molecular sieves, $B(OH)_3$, and $MgSO_4$ in the catalyzed reactions, *in situ*, failed to prevent hydrolysis of DBU.

Table 3 shows identical conversion, 60%, in all ratios of catalyst to substrate, demonstrating that the reaction is not mass transport limited under these conditions. This may also demonstrate that the reaction reaches an equilibrium under the conditions used.

Table 1. Catalytic Hydrogenation of [$DBUH^+$] Methyl Carbonate Using Different Homogeneous Catalysts

catalyst	DBU-MeOH ratio	sub/cat	temp (°C) (time)	conv (%) (MF)[c]	conv (%) (DF)[c]	total conv (%) (MF + DF)	TON
$RuCl_2(PPh_3)_3$	2:1	2160	110 (16 h)	0	24	24	510[a]
$RuCl_2(PPh_3)_3$	2:1	2160	140 (40 h)	33	1	34	750[a]
$RuCl_2(PPh_3)_3$	1:3	2160	140 (40 h)	45	16	61	1300[b]
$RuHCl(PPh_3)_3$	1:3	2080	140 (40 h)	42	8	50	1060[b]
$RuCl(OAc)(PMe_3)_4$	1:3	1130	110 (16 h)	7	17	24	270[b]
$RuCl(OAc)(PMe_3)_4$	1:3	1130	110 (40 h)	6	20	26	300[b]
$RuCl(OAc)(PMe_3)_4$	1:3	1130	140 (40 h)	20	28	48	540[b]
$FeCl_2(dmpe)_2$	1:3	960	140 (40 h)	18	2	20	200[b]

[a]Catalytic conditions: 514 mg (2.25 mmol) of [$DBUH^+$] methyl carbonate, 0.34 mL (2.25 mmol) of DBU, 1 mg (0.001 mmol) of $RuCl_2(PPh_3)_3$, 20 atm of H_2. [b]Catalytic conditions: 514 mg (2.25 mmol) of [$DBUH^+$] methyl carbonate, 0.18 mL (4.5 mmol) of methanol, 1 mg [0.001 mmol of $RuCl_2(PPh_3)_3$, 0.001 mmol of $RuHCl(PPh_3)_3$, 0.002 mmol of $RuCl(OAc)(PMe_3)_4$, or 0.002 mmol of $FeCl_2(dmpe)_2$] of catalyst, 20 atm of H_2. [c]Conversion is determined by NMR analysis of the reaction solutions; see Experimental Section. Relative uncertainties are estimated at ±5% based upon reproducibility of duplicate runs. DBU = 1,8-diazabicycloundec-7-ene. DF = [$DBUH^+$] formate. MF = methyl formate. MeOH = methanol.

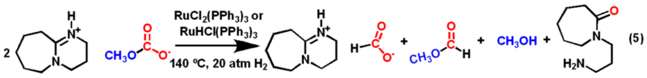


Figure 2. Conversion of DBU methyl carbonate to formate and methyl formate.

Table 2. Catalytic Activity of $RuCl_2(PPh_3)_3$ in Different Switchable Ionic Liquids

SWIL	temp (°C)	conv (%) (MF)	conv (%) (DF)	total conv (%) (MF + DF)	TON
DBU-MeOH (1:3)	110	3	11	14	310[a]
	140	45	16	61	1300[a]
DBU-*n*-propanol (1:3)	110	0	20	20	440
	140	26	9	35	770
DBU-*n*-hexanol (1:3)	110	0	10	10	230
	140	18	5	23	510

[a]Catalytic conditions.: 2.25 mmol of [$DBUH^+$] alkyl carbonate, 4.5 mmol of alcohol, 1 mg (0.001 mmol) of $RuCl_2(PPh_3)_3$, 20 atm of H_2. Relative uncertainties are estimated at ±5% based upon reproducibility of duplicate runs.

Table 3. Catalysis Profile of $RuCl_2(PPh_3)_3$ at Different Metal Loading[a]

catalyst	sub/cat	conv (%) (MF)	conv (%) (DF)	total conv (%) (MF + DF)	TON[b]
$RuCl_2(PPh_3)_3$	1080	46 ± 1	13 ± 1	59 ± 1	640 ± 5
$RuCl_2(PPh_3)_3$	2160	45 ± 1	16 ± 1	61 ± 1	1300 ± 10
$RuCl_2(PPh_3)_3$	4330	45 ± 2	15 ± 2	60 ± 2	2600 ± 50
$RuCl_2(PPh_3)_3$	8650	42 ± 1	17 ± 2	59 ± 1	5100 ± 50

[a]Catalytic conditions: 514 mg (2.25 mmol) of [$DBUH^+$] methyl carbonate, 0.18 mL (4.5 mmol) of methanol, an appropriate amount of $RuCl_2(PPh_3)_3$, 20 atm of H_2, 140 °C, 40 h. [b]Average of two runs. Absolute uncertainties are the difference between the two runs.

Table 4. Effect of CO_2 Pressure on the Catalytic Hydrogenation of [$DBUH^+$] Methyl Carbonate Using $RuCl_2(PPh_3)_3$ Catalyst[a]

catalyst	P_{H2} (atm)	P_{CO2} (atm)	conv (%) (MF)	conv (%) (DF)	total conv (%) (MF + DF)	TON
$RuCl_2(PPh_3)_3$	20	0	45	16	61	1300
$RuCl_2(PPh_3)_3$	20	13	56	13	69	1490
$RuCl_2(PPh_3)_3$	20	20	59	11	70	1510

[a]Catalytic conditions: 514 mg (2.25 mmol) of [$DBUH^+$] methyl carbonate, 0.18 mL (4.5 mmol) of methanol, 1 mg (0.001 mmol) of $RuCl_2(PPh_3)_3$, reaction temp 140 °C, reaction time 40 h. Relative uncertainties are estimated at ±5%.

The presence of additional CO_2 with H_2 leads to higher conversion to [$DBUH^+$] formate and methyl formate (Table 4). Without additional CO_2 pressure total conversion was 61% to [$DBUH^+$] formate and methyl formate, which can be increased up to 70% at a 20 atm pressure of CO_2. These results suggest that the availability of CO_2 in the reaction mixture may be catalytically acted upon, or alternatively the CO_2 gas may lead to a steady state of methyl carbonate once the original methylcarbonate is consumed in catalysis. A series of $^{13}C\{^1H\}$ NMR experiments were performed using a custom pressure-tolerant PEEK NMR cell (Figures S4–6) to identify the speciation of CO_2 under reaction temperatures (25–110 °C).[43] In these experiments, the $^{13}C\{^1H\}$ NMR spectrum showed 25% of the methyl carbonate remained in solution, with no detectable CO_2 in the liquid phase, indicating 75% of the CO_2 was in the gas phase (Figure S6). This experiment demonstrated that alkyl carbonates do not fully decompose at reaction temperatures and that physical solubility of CO_2 is too low to be detected via NMR under reaction conditions. In the reaction conditions, 2.25 mmol of [$DBUH^+$] methyl carbonate was used in a 10 mL cell at 110 °C. Assuming ideal behavior (and that 25% of the carbonate remains intact), we calculate at most a CO_2 partial pressure of 4.4 atm may be generated. Such a low partial pressure of CO_2 is not sufficient enough to force appreciable solubility of CO_2 in solution at 110 °C, as it is known that CO_2 physical solubility decreases with increases in temperature. The CO_2 solubility at 110 °C would be essentially negligible under reaction conditions. Such a concentration discrepancy would suggest that hydrogenation of the alkyl carbonate would be more likely, but we cannot disprove any direct CO_2 hydrogenation.

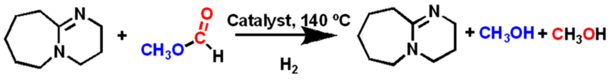
As alkyl carbonates and CO_2 are in equilibrium in SWILs, it is impossible to decouple the two species to decipher reactivity. Thus, to try to identify the reactive species, analogous systems where a carbonate or CO_2 was the sole species in solution were needed. Bicarbonate salts were chosen to elucidate the reactivity, as they are similar to alkylcarbonates. $NaHCO_3$ and $KHCO_3$ were not chosen, as they thermally disproportionate into CO_2, H_2O, and Na_2CO_3 and K_2CO_3, respectively, at temperatures used in this study (Table S2),[44] thus effectively providing both bicarbonate and CO_2. For this reason $CsHCO_3$

was chosen due to its higher decomposition temperature (~175 °C).[44]

Hydrogenations of $CsHCO_3$ using $RuCl_2(PPh_3)_3$ under comparable conditions showed modest conversion to $CsHCO_2$ with an equivalent amount of $CsCH_3OCO_2$ (Figure S7). All carbon-containing species were identified via $^{13}C\{^1H\}$ NMR spectroscopy (170.9 ($CsHCO_2$), 168.2 ($CsHCO_3$), 161.4 ($CsCH_3OCO_2$), and 53.9 ($CsCH_3OCO_2$)). The presence of $CsCH_3OCO_2$ suggests that the bicarbonate was converted into the methyl carbonate, and the hydrogenation may proceed via the methylcarbonate salt of cesium. Attempts to make and isolate $CsCH_3OCO_2$ from $CsHCO_3$ were unsuccessful; thus no direct hydrogenation studies of $CsCH_3OCO_2$ could be performed. The activity of $CsHCO_2$, albeit indirectly, suggests the combination of *both* alcohol and base may be required for a hydrogenation of CO_2 to methyl formate.

We proposed to close the cycle by hydrogenating methyl formate to methanol (Scheme 2). Hydrogenations of methyl formate to methanol have recently been shown by Sanford, Milstein, and Leitner to proceed with Bronsted acid and metal cocatalysts.[14−17,35] Our attempts to hydrogenate methyl formate directly to CH_3OH were performed under varied conditions; however no detectable conversion to methanol was observed using $^{13}C\{^1H\}$ NMR. The lack of activity is likely due to this system being base-promoted, which, to our knowledge, has yet to be demonstrated (Scheme 2). Attempts to identify conditions or catalysts that can promote a base-promoted hydrogenation of methyl formate are the focus of current work in our laboratory.

Scheme 2. Proposed Hydrogenation of Methyl Formate to Methanol from a Switchable Ionic Liquid



(8)

CONCLUSIONS

Using SWILs, CO_2 can be captured and chemically converted to an alkyl carbonate, hydrogenated to formate, and then esterified to methyl formate. The hydrogenations of alkyl carbonates are base-tolerant and proceed under the conditions of 110 °C and 20 atm of H_2. Raising the temperature to 140 °C promotes esterification of the produced DBU formate (with the liberated alcohol from the hydrogenation step), providing alkylformate and water, and releases the base. Hydrolysis of DBU observed during the esterification indicates bases that are susceptible to hydrolysis should be avoided for the esterification step in future studies. Speciation studies under reaction conditions suggest methyl carbonates are present in millimolar concentrations, far higher than undetectable concentrations of any evolved CO_2 from the carbonate that may be physically dissolved in solution at 110 °C. At this time the reactive species (i.e., alkyl carbonates or CO_2) cannot be identified, as the alkylcarbonate and CO_2 are in equilibrium in this system. Hydrogenations of $CsHCO_3$ to $CsHCO_2$ were successful in methanol, possibly via the observed $CsCH_3OCO_2$. The results from this study indicate that, at least with respect to SWILs, alkyl carbonates may be a substrate for hydrogenation, in addition to free CO_2. Availability of either CO_2 or the carbonate as the active species opens new doors for catalyst designs and reactive pathways for CO_2 that may have different selectivity or kinetic activity.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an N_2 atmosphere unless stated otherwise. The methyl formate, triphenylphosphine, $NaHCO_3$, $KHCO_3$, $CsHCO_3$, dmpe (1,2-bis(dimethylphosphino)ethane), and depe (1,2-bis(diethylphosphino)ethane) were purchased from Aldrich and used without further purification. DBU (Aldrich), methanol (Aldrich), propanol (Aldrich), and hexanol (Aldrich) were dried over sodium or 4 Å sieves. The syntheses of $RuCl_2(PPh_3)_3$,[45] $RuHCl(PPh_3)_3$,[46] $RuCl(OAc)(PMe_3)_4$,[47] and $FeCl_2(dmpe)_2$[48] were previously reported elsewhere. Heterogeneous catalysts 5 wt % Ru/C, 8.8 wt % Pd/Al_2O_3, and 4 wt % Pd/MCM-41 were prepared by using the wet impregnation and subsequent hydrogen reduction method. The supercritical fluid grade CO_2 (Praxair, SFE grade, 99.999%, H_2O <0.5 ppm) and ultrahigh pure grade H_2 gases were purchased from Oxarc and used as received. The gas was delivered to the tube directly from the tank through a stainless steel gas manifold line at specified pressures.

Acquisition of NMR Spectra. Proton and ^{13}C NMR spectra were collected on either 300 or 500 MHz Varian instruments. The ^{13}C spectra were collected using a 45 deg pulse, 0.865 s acquisition time, and a 1 s recycle time transient average set at 256. These parameters were found to yield highly reproducible results through testing with known concentrations of carbonate- and formate-containing solutions. Chemical shifts were referenced both externally to TMS and internally to residual DBU. Coupling constants are reported in hertz (Hz). The PEEK high-pressure NMR tubes were designed and built at Pacific Northwest National Lab.

Synthesis of [DBUH⁺] Methyl Carbonate. Dried DBU (3 mL, 20 mmol), methanol (0.8 mL, 20 mmol), and a stir bar were charged into a dried stainless steel vessel and pressurized to 1 atm with dry CO_2 at room temperature. A white powder was obtained, which was used for further hydrogenation reaction.

Hydrogenation of [DBUH⁺] Methyl Carbonate to [DBUH⁺] Formate and Methyl Formate. A 514 ± 3 mg (2.25 mmol) amount of [$DBUH^+$] methyl carbonate and 0.34 mL (2.25 mmol) of DBU or 0.18 mL (4.5 mmol) of methanol and 1 mg [0.001 mmol of $RuCl_2(PPh_3)_3$, 0.001 mmol of $RuHCl(PPh_3)_3$, 0.002 mmol of $RuCl(OAc)(PMe_3)_4$, or 0.002 mmol of $FeCl_2(dmpe)_2$] of catalyst were mixed in a stainless steel tube reactor. The catalyst was delivered from a stock solution (5 ± 0.1 mg/5 mL) in CH_2Cl_2 to yield an appropriate amount of catalyst. The CH_2Cl_2 was evaporated prior to addition of other reagents. The SS reactor, composed of a commercially available nominally 10 mL sample cylinder (total measured volume of 11 mL) equipped with a stir bar, was charged with 20 atm of H_2 at room temperature. The reaction mixture was heated to 110 or 140 °C while being stirred (200 rpm) for 16 or 40 h at reaction temperature. After the reaction, the autoclave was cooled with ice water and the pressure was slowly released after complete cooling. The reactor was opened in a glovebox, and the product was characterized via NMR analysis of the neat solution. [$DBUH^+$] propyl and hexyl carbonate were produced *in situ* by adding 1 atm of CO_2 for 30 min with stirring a 1:3 mixture of DBU and the alcohol and then removing the excess CO_2 under mild vacuum. NMR analysis of similar solutions showed almost complete conversion (of DBU) to the alkyl carbonate.

The $^{13}C\{^1H\}$ signals of the neat product solution for the bridgehead carbon on DBU and protonated DBU ([$DBUH^+$]) appear at the same position. The peak area of this peak was added to the peak area of the carbonyl carbon of any hydrolyzed DBU to give the total amount of DBU in the system. The conversion of [$DBUH^+$] methyl carbonate to [$DBUH^+$] formate was calculated by dividing the peak area for the formate carbon by the DBU total. Due to the high volatility of methyl formate (bp = 32 °C), some methyl formate was always lost during venting. Fortunately, for this analysis, the hydrolysis of DBU is complete under these reaction conditions, allowing the use of the peak area of the carbonyl carbon of the hydrolyzed DBU in place of methyl formate. The remaining methyl carbonate can be either directly measured in the $^{13}C\{^1H\}$ NMR spectrum or calculated by difference. The $^{13}C\{^1H\}$ NMR signals of the carbonyl carbons for formate, methyl formate, hydrolyzed DBU, and methyl carbonate, in addition to the signals for the bridgehead carbons for DBU and [DBUH$^+$], all are nonprotonated and show similar relaxation times, allowing direct comparison of the peak areas under the NMR conditions used. This was tested using known amounts of methyl formate, [DBUH$^+$] formate, DBU, and [DBUH$^+$] carbonate and found to be correct within 10%.

Hydrogenation of $NaHCO_3$, $KHCO_3$, or $CsHCO_3$ to Cs Formate. A 189 mg (2.25 mmol) portion of $NaHCO_3$, 225.3 mg (2.25 mmol) or 436.3 mg of $CsHCO_3$ (2.25 mmol), 0.9 mL (22.5 mmol) of methanol, and 1 mg (0.001 mmol) of $RuCl_2(PPh_3)_3$ were added into a stainless steel tube reactor. Next, the tube reactor was filled with 20 atm of H_2 at room temperature. The reaction mixture was heated to 110 °C and then was stirred (200 rpm) for 16 h at reaction temperature. After the reaction time, the autoclave was cooled with ice water and the pressure slowly released. The reactor solution was opened in a glovebox, and the product was characterized via NMR analysis as for the [DBUH$^+$] methyl carbonate.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables and supporting NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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