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The mechanism for production of abiogenic formate from CO_2 and lactate from glycerine: uncatalyzed transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions

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Recently, formate of possible abiogenic origin has been reported from uncatalyzed transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions. However, little is known about the mechanism for production of abiogenic formate from CO_2 and lactate from glycerine during such processes. Herein, we investigated the formation of abiogenic formate from CO_2, D_2O solvent effect, reactor materials effect and H_2O molecules catalysis for uncatalyzed transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions, and then have proposed and proved the potential reaction mechanism. The present work should help facilitate studies on industrial application of CO_2 reduction using abundant alcohol compounds as reducing materials rather than hydrogen, and the development of renewable high-valued chemicals from alternative biomass derivatives and the primary greenhouse gas to fossil fuel.

1. Introduction

In the current world, carbon dioxide (CO_2) arises mainly from combustion of fossil fuels and is regarded as the most significant greenhouse gas. Hence, it has recently attracted significant attention from the scientific community with environmental problems, such as the rapid growing of global warming and weather fluctuation.[1] CO_2, on the other hand, as an abundant, nontoxic, non-flammable, easily available, and renewable carbon resource, could be effectively reduced into useful organic products, and thus it would providea an environmentally friendly feedstock to be recycled and reused.[2-3] To compensate for its inherent thermodynamic stability and low energy level, significant efforts have been devoted to exploring technologies for CO_2 transformation in which high free energy content substances are required, such as hydrogen, unsaturated compounds, small-membered ring compounds and organometallics.[2-4] A promising approach in that regard seems to be the transformation of CO_2 into formic acid and its derivatives. Since Farlow and Adkins in 1935 reported the first direct hydrogen-transfer reduction of CO_2 into formic acid using H_2 as a reductant and Raney nickel as a catalyst,[5] it is of paramount importance from a standpoint of green chemistry to develop homogenous or heterogeneous metal catalysts for converting CO_2 into formic acid or formate salts.[1-4] Formic acid is an important chemical feedstock and is used as a synthetic precursor and a commercial product in the leather, agriculture and dye industries. In addition, it was demonstrated that formic acid might be used as a hydrogen storage system.[6-7] So far, formic acid is manufactured industrially mainly from toxic carbon monoxide and water by carbonylation of NaOH at elevated pressure and temperature. Compared with this traditional method, the process of obtaining formic acid from renewable CO_2 is safer, more sustainable and greener, and will be rapidly developed under the present situation. However, the production of CO_2-derived formic acid is not widely used in industrial chemical processes because the reductant, H_2, is currently produced from reactions of crude oil-derived methane with water. Therefore, it would be interesting and highly desirable to reduce CO_2 using an alternative substance rather than H_2.

Hydrothermal processes have been attracting increasing attention for use in organic chemical reactions, because high-temperature water (HTW) is an environmentally benign solvent compared to organic solvents and has remarkable properties as a reaction medium.[8-9] For example, HTW has a lower dielectric constant, fewer and weaker hydrogen bonds, and a higher isothermal compressibility than ambient liquid water. The solubility of most gases in liquid water initially decreases as the temperature is increased above ambient temperature, but a minimum solubility is soon reached, after which the gas solubility

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increases. For example, the minimal solubility of CO_2 occurs at around 150 °C.[9] Moreover, many organic reactions under ambient conditions only proceed in the presence of acidic/basic or metallic catalysts; however, these reactions can occur in HTW in the absence of an added catalyst.[10-13]

There is increasing interest in performing CO_2 reductions in HTW,[14-21] because in this medium, H_2 can be produced from metal or alcohol compounds. Horita and Berndt reported that CO_2 is converted to CH_4 by H_2, which is formed under hydrothermal conditions (≤400 °C, ≤100 MPa) in a process catalysed by a hydrothermally formed nickel-iron alloy. In this system, H_2 is produced during the conversion of olivine into serpentine and magnetite.[14] It has also been found that formic acid can be hydrothermally produced from CO_2 with Fe-powder and/or Ni-powder.[14-19] He et al. have used iron nanoparticles not only as reducing agents but also as catalysts to transform CO_2 into formic acid and acetic acid.[18]

On the other hand, biomass is an abundant source of alcohols in the form of carbohydrates and polyols such as cellulose, starch, and glycerine.[22-23] Moreover, glycerine has been a potentially important biorefinery feedstock as a byproduct of biodiesel production. Our recent research showed that in HTW, CO_2 is reduced to formate by the alcohol-mediated reduction using isopropanol or glycerine as alcohol model compounds.[20-21] Like hydrogen-transfer reduction of CO_2 with H_2, these reactions are endergonic ($\Delta GRT > 0$), but a hydrogen transfer reduction of CO_2 with glycerine require much less energy ($\Delta GRT < 0$) (Eqs. 1,4); and addition of a base improves the enthalpy of the reaction, while dissolution of the gases improves the entropy (Eqs. 2,3,5,6). We found that CO_2 could be effectively converted into formate using glycerine as a reducing agent, and the molar yield of formate was almost equal to that of lactate from glycerine.[21] However, little is known about the mechanism for production of abiogenic formate from CO_2 and lactate from glycerine during such processes. More recently, we have also proved that glycerine was first transformed to acetol via a dehydration reaction and a keto-enol tautomerization reaction during the production of hydrogen and lactic acid from glycerine.[24] Herein, we investigated the formation of abiogenic formate from CO_2, D_2O solvent effect, reactor materials effect and H_2O molecules catalysis for uncatalyzed transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions, and then have proposed and proved the potential reaction mechanism. The present work should help facilitate studies on industrial application of CO_2 reduction with abundant alcohol compounds as reducing materials rather than hydrogen, and the development of renewable high-valued chemicals from alternative biomass derivatives and the primary greenhouse gas to fossil fuel.

$$CO_{2(g)} + H_{2(g)} \xrightarrow{32.9kJ/mol} HCOOH_{(l)} \quad (1)$$

$$CO_{2(g)} + H_{2(g)} + NH_{3(aq)} \xrightarrow{-9.5kJ/mol} HCOO^-_{(aq)} + NH^+_{4(aq)} \quad (2)$$

$$CO_{2(aq)} + H_{2(aq)} + NH_{3(aq)} \xrightarrow{-35.4kJ/mol} HCOO^-_{(aq)} + NH^+_{4(aq)} \quad (3)$$

$$C_3H_5(OH)_3 + CO_{2(g)} \xrightarrow{-13kJ/mol} CH_3CH(OH)COOH_{(aq)} + HCOOH_{(l)} \quad (4)$$

$$C_3H_5(OH)_3 + CO_{2(g)} + NH_{3(aq)} \xrightarrow{-55.3kJ/mol} CH_3CH(OH)COOH_{(aq)} + HCOO^-_{(aq)} + NH^+_{4(aq)} \quad (5)$$

$$C_3H_5(OH)_3 + CO_{2(aq)} + NH_{3(aq)} \xrightarrow{-81.2kJ/mol} CH_3CH(OH)COOH_{(aq)} + HCOO^-_{(aq)} + NH^+_{4(aq)} \quad (6)$$

2. Experimental section

2.1 Materials

Glycerine (99%) was used as the test material. NaOH (96%) and $NaHCO_3$ (99%) were used as alkaline catalysts. Dry ice (99%) and $NaHCO_3$ were used as CO_2 sources. Glycerine, NaOH, $NaHCO_3$, dry ice and formic acid (99.9%) were obtained from Sinopharm Chemical Reagent Co., Ltd, China. Other chemicals, such as $NaH^{13}CO_3$ (99% ^{13}C), D_2O (99.9% D), acetol (99%), pyruvaldehyde (99%) and L+lactate (99%) were supplied by Sigma-Aldrich (Shanghai) Trading Co., Ltd, China.

NaOD used were prepared by dissolving the solid base in deuterium oxide followed by drying in a rotary evaporator, and then repeated the process three times. Although the resulting NaOD solid contained some residual ^1H, the amount of ^1H introduced into the reaction mixture was negligible as only a small quantity of base relative to the deuterium oxide solvent was used in each reaction. $NaDCO_3$ used in this investigation were prepared by aerating excess CO_2 in Na_2CO_3 solution of deuterium oxide for 2 h and then drying in a rotary evaporator.

Most experiments were performed in a batch type reactor made of stainless steel 316 tubing (3/8 inch diameter, 1-mm wall thickness, 120-mm length) with two end fittings, providing an inner volume of 5.7 mL.[19] The reactor can collect gas by a nozzle and high-pressure valve. The reaction temperature was controlled by a salt bath. In a few cases, a batch reactor with a Teflon inner wall having an inner volume of 20 mL was used in order to investigate the effect of the reactor materials.

2.2 Experimental Procedure

The typical procedure of hydrothermal reactions is described as follows: A 4 mL water mixture with 0.33 M glycerine, 0-2.5 M NaOH (or NaOD) and 0-0.44g dry ice (CO_2) or 0-1.76g $NaHCO_3$ (or $NaDCO_3$) was added to the batch reactor, and then the reactor was put into a salt bath preheated to a desired temperature. In the salt bath, the reactor was shaken while being kept horizontally, to mix well and enhance heat transfer. After a desired reaction time, the reactor was removed from the salt bath and put into a cold-water bath to quench the reaction. The reaction time was defined as the period during which the reactor was kept in the salt bath. The real reaction time is shorter than the apparent reaction time, because the heat-up time to raise the temperature of the reaction media from 20 to 300 ºC was about 15 s. The temperature of the salt bath was taken as the reaction temperature. After cooling, samples of the liquid phase and gas phase in the reactor were collected for analysis. In all experiments, we fixed the temperature at 300 ^oC and water filling rate at 70%. So, the reaction pressure was about 9 MPa, which could be estimated from the water saturation pressure at 300 ^oC.

In order to investigate the effect of the reactor materials on the hydrothermal reactions, a batch reactor with a Teflon inner wall having an inner volume of 20 mL was used, which had been described elsewhere.[13] The typical reaction procedure by using this reactor is as follows. An 14 mL mixture with 0.33 M glycerine, 1.40g NaOH and 1.54g CO_2 was put into the reactor. After being sealed, the reactor was placed in an electric furnace that had been preheated to 300 °C. After the desired reaction time, the reactor was removed from the electric furnace for cooling at room temperature (25°C). Then, liquid samples were collected for HPLC analysis.

2.3 Product analysis

After the reactions, the liquid samples were collected for ^1H- and

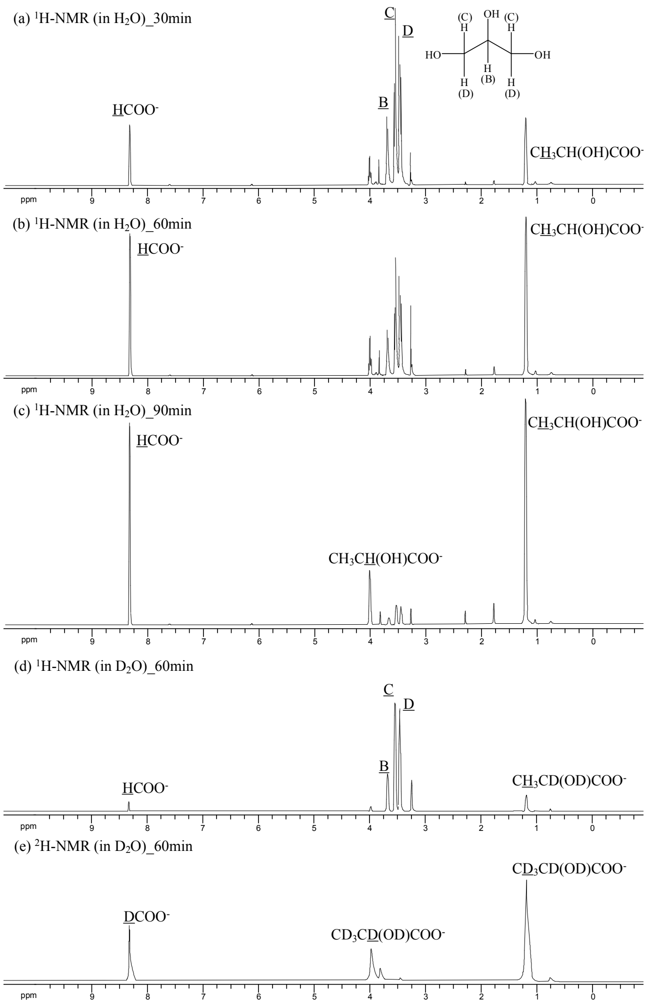


Fig. 1 ^{1}H-NMR spectra for the solution after the hydrothermal reaction of 0.33 M glycerine at 300 °C with 0.40g NaOH and 0.44g CO_2 in H_2O for (a) 30 min, (b) 60 min, (c) 90 min, and (d) ^{1}H-NMR and (e) ^{2}H-NMR spectra with 0.41g NaOD and 0.44g CO_2 in D_2O for 60 min.

^{2}H-NMR, ^{13}C-NMR, LC-MS and HPLC analyses, and gas samples were collected for GC analysis. Peak identification was accomplished by comparing the sample peak retention time with those of standard solutions of pure compounds. All quantitative data reported in this study were the average values of the analytical results of at least three samples with the relative errors always less than 10% for all experiments.

NMR Analysis. ^{1}H-, ^{2}H- and ^{13}C-NMRs were performed using a NMR spectrometer (DMX 500, 500 MHz). In order to reduce the signal interference from the large number of solvent water, 40 μl collected liquid samples were put into 5 mm i.d. NMR tubes and then were deal with through the freeze-drying process. After freeze-drying, 0.5 ml D_2O were added into the samples NMR tubes for ^{1}H-NMR analyses, or into 0.5 ml H_2O for ^{2}H-NMR analyses.

LC-MS Analysis. Liquid chromatography was performed on a Shimadzu LC-10AD HPLC system consisting of an autosampler (SILHTc). The HPLC was coupled to a Shimadzu LCMS-2010A single quadrupole mass spectrometer with an electrospray ionization (ESI) interface. Data acquisition and processing were accomplished using Shimadzu LC-MS solution software for LC-MS-2010 high-performance liquid chromatography/mass spectrometer. LC-MS conditions are shown as follows: Column, RSpak KC-811 (300 × 8.0 mm I.D., Shodex Packed Corporation, Japan); Mobile phase, 1 mM $HClO_4$; Flow rate, 0.25 mL/min; detection, UV 210 nm; Column temperature, 50 ºC; MS, negative mode (scan range, *m/z* 30-120); Ionization, ESI.

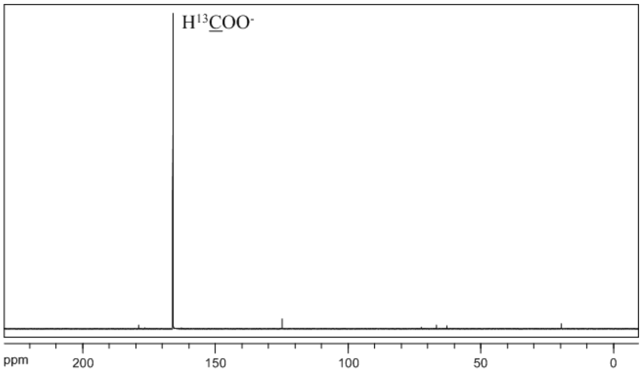


Fig. 2 ^{13}C-NMR spectra for the solution after the hydrothermal reaction of 0.33 M glycerine at 300 °C with 0.89 g $NaH^{13}CO_3$ in H_2O for 90 min.

HPLC analysis. The liquid samples were filtered through a 0.45 mm filter, and then were adjusted with sulfuric acid until the pH values of the solution reached 2-3. After that, the liquid samples were analyzed by HPLC. HPLC analysis was performed using an Agilent 1200 HPLC system equipped with a tunable absorbance detector (UV detector) and a differential refractometer (RI detector). During the HPLC analysis, two columns (RSpak KC811) were used in series, and the solvent used was 1 mM $HClO_4$ at a flow rate of 1.0 mL/min.

GC analysis. The gas sample was analyzed by an Agilent 7890 GC with a Porapak Q column or a POLA column.

3. Results and discussion

3.1 Formation of abiogenic formate from CO_2

Fig.1 shows the ^{1}H- and ^{2}H-NMR spectra of the solutions after the hydrothermal reactions of glycerine with NaOH and CO_2 in H_2O (or NaOD and CO_2 in D_2O) at 300 ºC. From a comparison of the time-dependent spectra of (a), (b) with (c) in Fig. 1, it can be seen that the gradual consumption of the reactant glycerine was accompanied by the production of high-valued lactate and formate. The transformation of glycerine into lactate was almost completed in 90 min under alkaline hydrothermal conditions, and the increase in reaction time from 30 min to 90 min resulted in a monotonous increase in the production of formate. Although a set of comparative experiments with or without CO_2 source suggested that the formate was produced from CO_2 in Fig. X1, but it might be from organic acids because it been reported that formic acid can be produced by decomposition of lactic acid.[25-26] So, in order to further acknowledge the production of abiogenic formate from CO_2, an experiment was carried out by using 0.89 g $NaH^{13}CO_3$ as a CO_2 source with 0.33 M glycerine in H_2O at 300 °C for 90 min. The collected liquid sample was adjusted with sulfuric acid until the pH values of the solution reached 2-3, and then was detected by ^{13}C-NMR analysis. As shown in Fig. 2, the produced formate ($H^{13}COO^-$) was observed at 165 ppm. These results suggested that CO_2 was indeed converted into abiogenic formate, and at the same time glycerine was transformed into lactate during such processes.

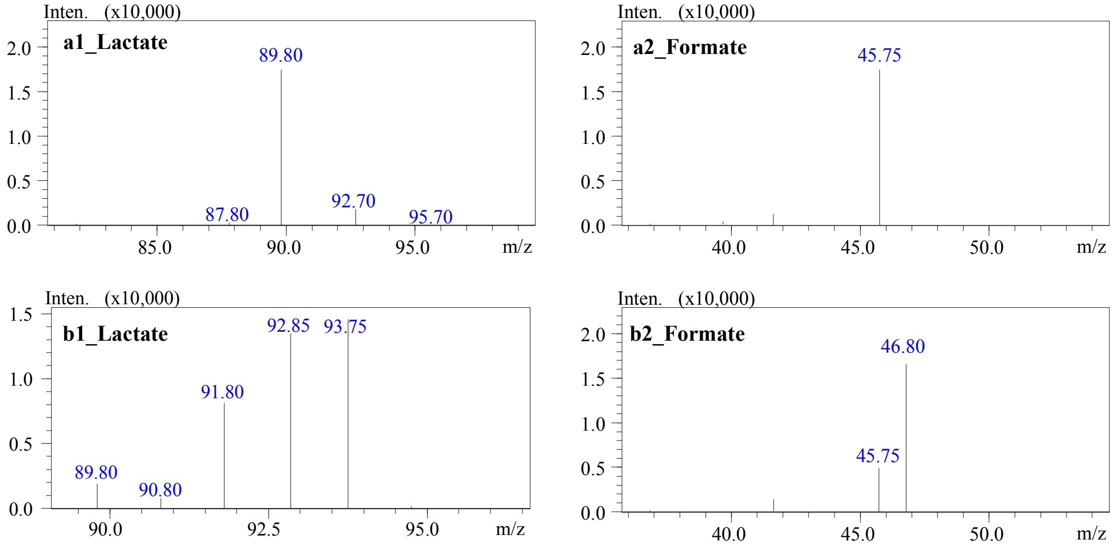


Fig.3 MS spectra of the lactate and formate solutions after the hydrothermal reactions of 0.33 M glycerine at 300 ºC with (a) 0.40g NaOH and 0.44g CO_2 in H_2O and (b) 0.41g NaOD and 0.44g CO_2 in D_2O.

3.2 Effect of D_2O solvent

To investigate the solvent isotope effect during the production of abiogenic formate from CO_2 and that of lactate from glycerine under alkaline hydrothermal conditions, we carried out a deuterium transformation study using 0.41 g NaOD and 0.44 g CO_2 in D_2O instead of 0.40 g NaOH and 0.44 g CO_2 in H_2O,[24] and the results are displayed in the ^{1}H- and ^{2}H-NMRs in Fig. 1 (d) and (e), respectively. By comparing spectrum (a) and (d) to (e) in Fig. 1, it can be observed that the Hs on the β-C of lactate has been almost transformed into D when in D_2O, and remaining glycerine do not take place H/D exchange reaction. However, it has been reported that simple alcohols do not participate in H/D exchange reactions, whereas the α-C of carboxyl groups undergo rapid and nearly complete exchange.[12,27] From these results, we can speculate that there is an intermediate product, such as R_1-CO-R_2, formed during the production of lactate from glycerine because of the H/D exchange on the β-C of lactate.

To further understand the deuterium behavior in the formation of lactate from glycerine in D_2O under alkaline hydrothermal conditions, the liquid samples obtained from the reaction of 0.41 g NaOD and 0.44 g CO_2 in D_2O at a temperature of 300 ºC were also analyzed by LC-MS. As shown in Fig. 3 (a1) and (b1), the m/z of lactate after reacting in H_2O was 89.80, but that after reacting in D_2O increased to 91.80, 92.85, and 93.75. This result from the LC-MS analysis is consistent with that of the previous NMR analysis, where a large number of Hs on the β-Cs of lactate were indeed exchanged by D in D_2O. These results suggest that the hydroxyl (-OH) group on the 2-C of glycerine converted to a carbonyl (C=O) group and then was reverted back into a -OH group in α-C of lactate.

3.3 Effect of reactor materials

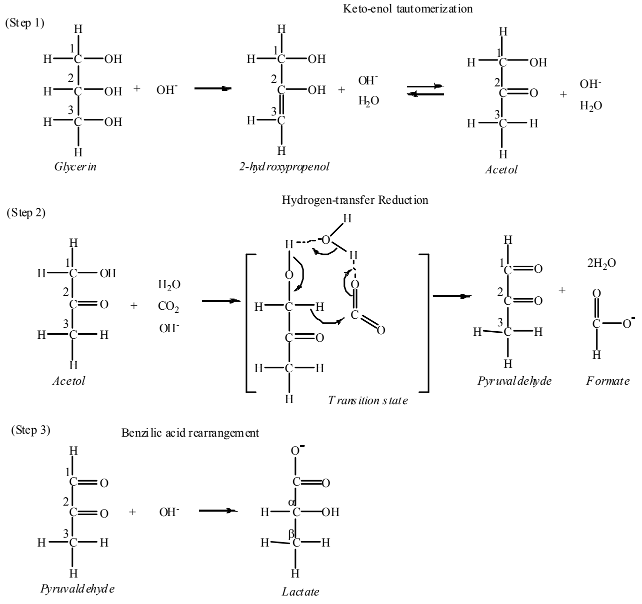
It is well known that SUS 316 material contains some metals, such as Fe, Ni, Mo and Cr. Recently, it was reported that formic acid can be produced from CO_2 via the oxidation of a zero-valent metal under hydrothermal conditions.[14-19] So, metals in SUS 316 reactor used in this study may play a catalytic role during transfer hydrogenation of CO_2 into formate with glycerine under alkaline hydrothermal conditions. In order to investigate the catalysis effect of reactor materials on the transfer hydrogenation of CO_2 with glycerine under hydrothermal alkaline conditions, we performed a series of experiments with a Teflon-line batch reactor with or without the addition of a small amount of SUS316 scrap. After 24 h at 200 °C with 0.33 M glycerine with 1.40g NaOH and 1.54g CO_2, the results showed that the formate and lactate yields with or without pieces of SUS316 were almost the same as shown in Table X1. This result suggests that catalytic effect of the reactor material is not obvious.

3.4 Catalysis of H_2O molecules

It is likely that water molecules are acting as a catalyst for transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions because of no significant catalytic effects of reactor material. To prove this, we carried out two anhydrous experiments with glycerine and dry ice at 300 °C using diethylamine or NaOH as a base, and we found that neither formate nor lactate was produced. However, both formate and lactate were detected by HPLC analysis in a hydrous experiment with glycerine and dry ice at 300 °C when diethylamine was used as a base. These results indicate that H_2O other than NaOH may catalyse the reaction of transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions. It has been also reported that addition of small amounts of water in organic solvent could accelerate the reduction of CO_2.[28-29] Moreover, Nguyen and Ha reported that water and CO_2 interacting in such a way have been calculated by ab initio methods to be more stable than the two species apart.[30]

3.5 Proposition of reaction mechanism

An outline of a potential mechanism is provided on transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal



Scheme 1. Potential mechanism for transfer hydrogenation of CO_2 with glycerine from glycerine under hydrothermal conditions.

conditions, on the basis of the above isotope effect of solvent, the catalytic role of water molecules, the almost same yields of lactate and formate and the detected pyruvaldehyde in Fig. X1. As shown in Scheme 1, in the first step, glycerine is dehydrated to produce 2-hydroxypropenol in E2 mechanism via a base attacking at the hydrogen of C-2 and then OH^- elimination of C-1. Subsequently, acetol is formed by keto-enol tautomerization of the produced 2-hydroxypropenol. In the second step, two hydrogen bonds may be formed among three molecules (acetol, H_2O, and CO_2), which makes the carbonyl-carbon on CO_2 and the hydride ion on the acetol even more positive. Next, the hydride ion attacks the carbonyl-carbon, and a cyclic transition state may be formed. Finally, pyruvaldehyde and formate are formed, and a water molecule is regenerated after an intramolecular hydride shift. In the third step, pyruvaldehyde undergoes a benzilic acid rearrangement to form the lactate salt. In the proposed pathway, water molecules make a hydrogen-bond ring network with the substrate molecules, and the eight-membered ring transition state greatly lowers the energy for bond cleavage and formation. Similar water-catalysed mechanisms have been proposed in which hydrogen bonding between the substrates and water molecules forms a ring transition state in the reaction.[10-13] Furthermore, it was reported that uncatalyzed Meerwein-Ponndorf-Verley (MPV) reduction could be achieved under hydrothermal conditions by using water molecules as catalysts.[31-33]

Additionally, it has been long considered that hydrogen-transfer reactions are reversible, such as MPV reduction and Oppenauer oxidation. Our previous work indicated that reaction of acetone and formic acid and reaction of isopropanol and CO_2 is a pair of reversible reactions.[13,20] Similarly, Farlow and Adkins in 1935 reported the first direct synthesis of formic acid from CO_2 and H_2 using Raney nickel catalyst (Eq. 7: $CO_2 + H_2 \rightarrow HCOOH$),[5] and Inoue et al. in 1976 discovered that the formic acid decomposed to CO_2 and H_2 once the pressures of these gases are reduced because catalysts for reaction 7 are also catalysts for the reverse reaction.[28] On transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions, however, after of hydrogen-transfer reactions, the formed pyruvaldehyde was further transformed into more stable lactate via a benzilic acid rearrangement, which thereby slowing the inverse reaction and then achieving a higher lactate yield.

Table 1. Comparison of the lactate yields from pyruvaldehyde and acetol

	Pyruvaldehyde [a]	Acetol [b]
Lactate (%)	96.7	59.6
Formate (%)	-	42.3
Remaining (%)	Trace	Trace

a: Pyruvaldehyde 0.33 M; NaOH 1.25 M; CO_2 0.44g; Temp. 300 ºC; Time 1.5 min.
b: Acetol 0.33 M; NaOH 1.25 M; CO_2 0.44g; Temp. 300 ºC; Time 1.5 min.

3.6 Testing of reaction mechanism

From the postulated mechanism shown in Scheme 1, we can presumed that H_2 decreases substantially because the hydride ion attacks the CO_2 rather better than H_2O by adding of CO_2. As shown in Table X2 (a) to (b) and (c), H_2 yields decreased to 4.0% and 3.8% from 84.5% by adding to CO_2 or $NaHCO_3$. Moreover, from the postulated mechanism shown in Scheme 1, we can presumed that H/D exchange was achieved in C-3 position because of ketone carbonyl group of acetol similar to C-1 position of acetol. In an independent run, we confirmed that $HCOO^-$ cannot be transformed into $DCOO^-$ in D_2O under solely alkaline hydrothermal conditions. From these above, we can predict that in D_2O reactions, the produced formate included $DCOO^-$ and $HCOO^-$, and furthermore $DCOO^-$ was more than $HCOO^-$, because of rapid and nearly complete H/D exchange under hydrothermal conditions.[12, 27] So, in order to detect D in the produced formate, the liquid sample obtained from the reaction of glycerine with NaOD and CO_2 in D_2O (or NaOH and CO_2 in H_2O) at a temperature of 300 ºC were analyzed by ^{2}H-NMR and LC-MS. By comparing spectrum (b) and (d) to (e) in Fig. 1, it can be observed that the Hs on formate have been almost transformed into Ds when in D_2O solvent. This result from the H-NMR analysis is consistent with that of the next LC-MS analysis. Uniformly, it can be seen in Fig. 3 (a2) and (b2) by LC-MS analyses that the m/z of formate after reacting in H_2O was 45.75, but that after reacting in D_2O was 45.75 and 46.80. The presence of large amounts of D in the produced formate straightforwardly indicates that acetol was formed in the first place as the most probable intermediate.

According to the proposed mechanism shown in Scheme 1, pyruvaldehyde and acetol could be regarded as the two key intermediates on transfer hydrogenation of CO_2 with glycerine under hydrothermal alkaline conditions. Therefore, we investigated the possibilities for producing lactate from pyruvaldehyde and acetol under the hydrothermal alkaline conditions. As shown in Table 1, the yield for lactate from 0.33 M pyruvaldehyde was 96.7% at 300 ^{o}C with 1.25 M NaOH and 0.44g CO_2 for reaction time of 1.5 min. Additionally, when an experiment with 0.33 M acetol, 1.25 M NaOH and 0.44g CO_2 was performed under hydrothermal conditions at 300 °C with after 1.5 min, the yields of lactate and formate were only 59.6%

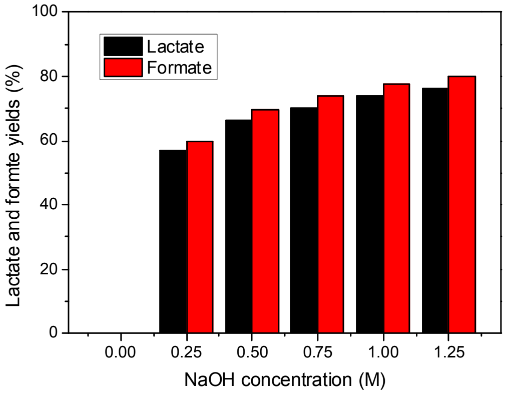


Fig. 4 Lactate and formate yields after the hydrothermal reactions of 0.33 M glycerine and 0.44g dry ice with 0-2.5 M NaOH at 300 ºC for 60 min.

and 42.3% shown in Table 1. In the reaction of acetol and CO_2, the yields of lactate and formate were relatively low because of the impact of the aldol condensation of acetol. Table 1 corroborates this presumption by showing lactate to be the major product obtained from pyruvaldehyde and acetol under these conditions.

3.7 Verification of Alkaline Role

Although the dehydration and keto-enol tautomerization reactions occur regularly in acid-catalyzed conditions, these reactions have also been reported in basic-catalyzed conditions.[34-36] The benzilic acid rearrangement occurs only in a basic solution. Furthermore, it has been recognized that addition of a base improves enthalpy of the reduction reaction of CO_2 and dissolution of the gases improves the entropy (Eqs. 2,3,5,6).[28-29] Thus, transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions must be critically dependent upon the concentration of the base. To confirm this alkaline role, experiments were performed with glycerine and 0.44 g CO_2 at 300 °C varying the NaOH concentration from 0 to 1.25 M. As shown in Fig. 4, both lactate and formate were not formed when the NaOH concentration was 0 M. However, the lactate and formate yields did increase sharply with an increase in the NaOH concentration. These results strongly support the proposed mechanism for transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions shown in Scheme 1.

3.8 Alkaline Hydrothermal Conversion Routes of Lactate and Intermediates

As shown the proposed mechanism in Scheme 1, one mole of glycerine and one mole CO_2 would generate one mole of lactate and one mole of formate through the following stoichiometric reaction 8:

$$C_3H_8O_3 + CO_2 + 2OH^- \rightarrow C_3H_5O_3^- + HCOO^- + 2H_2O \quad (8)$$

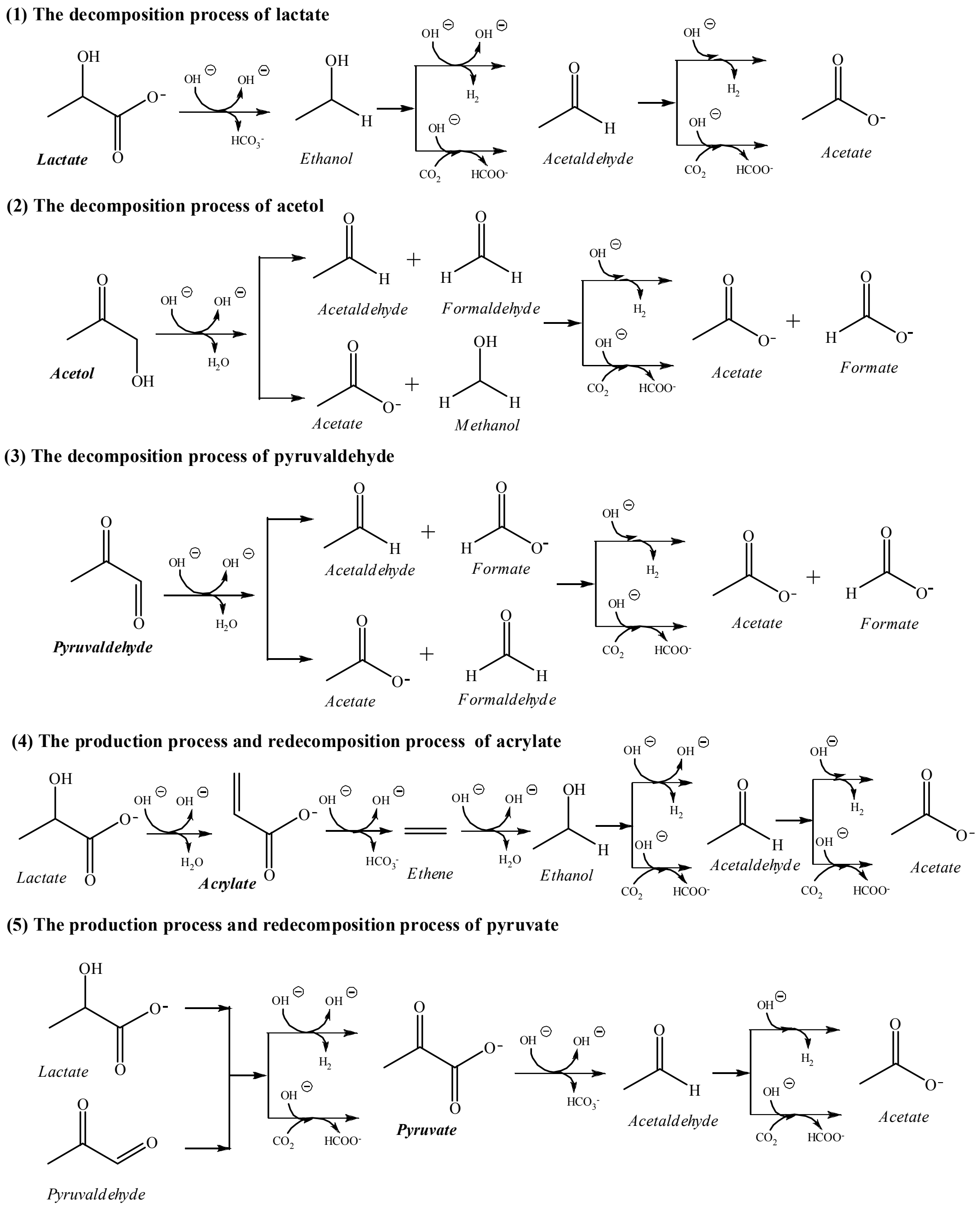
HPLC chromatograms of the reaction mixture after a reaction carried out at 300 °C, with glycerine and 0.25 M NaOH with or without dry ice (CO_2 source) for 60 min is shown in Fig. X1. As it can be seen in Fig. X1, pyruvate, pyruvaldehyde, acrylate, formate and acetate were detected in addition to lactate. According to the proposed mechanism in Scheme 1, acetol and pyrvaldehyde are intermediates on the hydrogen-transfer reduction of CO_2 with glycerine, but acetol was not detected in Fig. 1 and X1. Based on all these findings, several alkaline hydrothermal conversion routes of lactate and reaction intermediates can be envisioned, which are given in Scheme 2.

These routes are not intended to be the only ones existing but several of the more probable. Route 1 is that under hydrothermal alkaline conditions, lactate was firstly decarbonized into produce acetaldehyde, which further oxidated into acetate by H_2O and CO_2 through ethanol and acetaldehyde as intermediates. Route 2 and 3 are that formate and acetate were finally formed from the oxidative cleavage of acetol and pyruvaldehyde under alkaline conditions through methanol, formaldehyde and acetaldehyde as intermediates. Route 4 is that acrylate produced from dehydration of lactate, was further decarbonized to form ethene, and then was oxidized into acetate by H_2O and CO_2 through ethanol and acetaldehyde as intermediates. Route 5 is that produced pyruvate from oxidative of pyruvaldehyde and lactate under alkaline conditions, was further decarbonized into acetaldehyde, which was finally oxidated into acetate by H_2O and CO_2.

From proposed mechanism in Scheme 1 and routes 1 to 5 in Scheme 2, we could deduce that addition of CO_2 can accelerate the conversion of glycerine into lactate, and slower the decarbonization of oxidative cleavage of C3 compounds into C1 and C2 compounds. From it can be seen from Table X2, acetate yield was greatly decreased by adding of CO_2 or $NaHCO_3$. Although formate yield was rapidly increased owing to reduction of CO_2, it suggested that on the contrary the amount of formate from decomposition of C3 compounds was affirmatively decreased. Interestingly, the peak area of pyruvate in Fig. X1 (b) increased greatly compared to that in Fig. X1 (a), and that of acrylate relatively decreased. As shown in Table X2 (a) and (b), pyruvate yield increased to 2.5% from 0.64% by adding 0.44 g CO_2, and acrylate yield decreased to 0.5% from 2.2%. It is because that although pyruvate was formed by the consecutive oxidation from pyruvaldehyde in addition to from lactate,[37] pyruvate may be mainly obtained from hydrogen-transfer reduction of lactate and CO_2 because 2-hydroxyl group in lactate seems to act as that in acetol. As side reactions of routes 1 to 5 in Scheme 2, these results also support the reaction mechanism in Scheme 1.

Conclusions

We have reported the formation of abiogenic formate from CO_2, D_2O solvent effect, reactor materials effect and H_2O molecules catalysis for uncatalyzed transfer hydrogenation of CO_2 with glycerine under alkaline hydrothermal conditions. Abiogenic formte was formed by transfer hydrogenation of CO_2 with glycerine, and glycerine was almost completely converted into lactate with the same excellent yield of formate. A discussion on the potential mechanism for transfer hydrogenation of CO_2 with glycerine suggests that in the first step, glycerine is conversed into acetol via a dehydration and a keto-enol tautomerization. In the second step, two hydrogen bonds may be formed among three molecules (acetol, H_2O, and CO_2), which makes the carbonyl-carbon on CO_2 and the hydride ion on the acetol even more positive. Next, the hydride ion attacks the carbonyl-carbon, and a cyclic transition state may be formed. Finally, pyruvaldehyde and formate are formed, and a water molecule is regenerated after an intramolecular hydride shift. In the third step, pyruvaldehyde



Scheme 2. Alkaline hydrothermal conversion routes of lactate, aectol, pyruvaldehyde, acrylate and pyruvate.

undergoes a benzilic acid rearrangement to form the lactate salt. The present work should help facilitate studies on industrial application of CO_2 reduction with abundant alcohol compounds as reducing materials rather than hydrogen, and the development of renewable high-valued chemicals from alternative biomass derivatives and the primary greenhouse gas to fossil fuel.

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