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Solvent Isotope Effect on Hydrogen-Transfer Reduction of CO_2 into Formate with Glycerine by Alkaline Hydrothermal Reaction

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Abstract: To examine the solvent isotope effect on hydrogen-transfer reduction of CO_2 into formate with glycerine by alkaline hydrothermal reaction, intermediates were identified by ^{13}C-NMR, ^{1}H-NMR, ^{2}H-NMR, LC-MS analyses. The results showed that (1) CO_2 was indeed converted into abiogenic formate; (2) a ketone carbonyl group as intermediate product was formed on hydrogen-transfer reduction of CO_2 into formate with glycerine by alkaline hydrothermal reaction; (3) acetol was the most probable intermediate in the first reaction by undergoing a dehydration rather than a dehydrogenation.

Keywords: CO_2, glycerine, solvent isotope effect, alkaline hydrothermal reaction.

1. INTRODUCTION

Highly efficient resourcing of CO_2 has become an important research area because of the position of CO_2 as the primary greenhouse gas and its great potential to become an important feedstock and reagent for organic transformations [1, 2]. In the search for the transformation of CO_2, one preliminary issue has to be taken into account: high free energy content substances are required to compensate for its inherent thermodynamic stability and low energy level, such as hydrogen, metals, unsaturated compounds, small-membered ring compounds, organometallics and alcohol compounds. Biomass is one of the most promising substances because of a lot source of alcohols in the form of carbohydrates and polyols [3, 4]. Furthermore, glycerine is a main candidate to be used as a building block especially in chemical synthesis as a three-carbon source and a byproduct of biodiesel production.

More recently, we found that on hydrogen-transfer reduction of CO_2 into formate with glycerine by alkaline hydrothermal reaction, CO_2 was transformed into formate and all the same glycerine could be effectively converted into lactate [5]. As shown as in stoichiometric reaction (1), one mole of formate and one mole of lactate would be generated from one mole of CO_2 and one mole of glycerine. Both formate and lactate are important chemical feedstock as synthetic precursors, and moreover lactate is receiving attention as a material for producing biodegradable lactic acid polymers. Herein, intermediates were identified by ^{13}C-NMR, ^{1}H-NMR, ^{2}H-NMR, LC-MS analyses to examine the solvent isotope effect on hydrogen-transfer reduction of CO_2 into formate with glycerine by alkaline hydrothermal reaction.

$$C_3H_5(OH)_3 + CO_2 + 2NaOH \longrightarrow CH_3CH(OH)COO \bullet Na + HCOO \bullet Na + 2H_2O \qquad (1)$$

2. EXPERIMENTAL PROCEDURE

Glycerine (99%), NaOH (96%), formic acid (99.9%), $NaHCO_3$ (99%) and dry ice (99%) were provided by Sinopharm Chemical Reagent Co., Ltd, China. D_2O (99.9% D), $NaH^{13}CO_3$ (99% ^{13}C) and acetol (99%) were supplied from Sigma-Aldrich (Shanghai) Trading Co., Ltd, China. NaOD was obtained by dissolving the solid base in D_2O and then drying in a rotary evaporator. $NaDCO_3$ was obtained by aerating superfluous CO_2 in Na_2CO_3 D_2O solution for 2 h and then drying in a rotary evaporator.

A 4 mL mixture of 0.33 M glycerine, 0.40g NaOH (or 0.41g NaOD) and 0.44g dry ice (CO_2) or 0.88 $NaHCO_3$ (or 0.89 $NaDCO_3$) in H_2O (or D_2O) were put into a batch-type reactor. The reactor used in this study was a Swagelok SUS 316 tube, sealed with two caps. The outside diameter of the reactor was 3/8 inch diameter, wall thickness 1 mm, length 120 mm, and capacity 5.7 mL. The reaction temperature was controlled using a molten salt bath. In the salt bath, the reactor was shaken while being kept horizontally, to mix well and enhance heat transfer [5]. After a desired reaction time, the reactor was removed from the salt bath and put into

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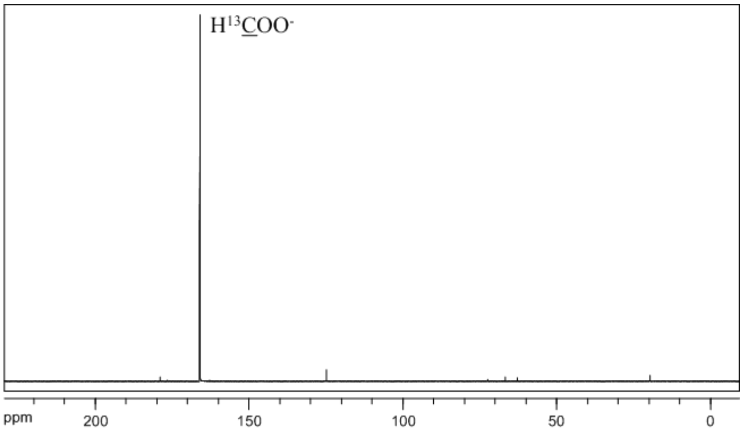

Figure 1: ^{13}C-NMR spectrum of collected liquid sample after the hydrothermal reaction with 0.89 g NaH^{13}CO$_3$ and 0.33 M glycerine in H_2O at 300 °C for 90 min.

a cold-water bath to quench the reaction. After the reactions, the collected liquid samples were analyzed by ^{1}H- NMR and ^{2}H-NMR, ^{13}C-NMR (BRUKER DMX 500, 500 MHz, Germany) and LC-MS (Shimadzu 2010A, Japan).

3. RESULTS AND DISCUSSION

3.1. ^{13}C-NMR Analyses on Hydrogen-Transfer Reduction of CO_2 into Formate with Glycerine by Alkaline Hydrothermal Reaction

It has been reported that formic acid was formed by decarboxylation of C3 compounds on the conversion of glycerine into lactate under hydrothermal alkaline conditions, such as lactic acid or acrylic acid [6]. So, we carried out an experiment with 0.33 M glycerine in H_2O at 300 °C for 90 min by using 0.89 g NaH^{13}CO$_3$ instead of NaH^{12}CO$_3$. The collected liquid sample was detected by ^{13}C-NMR analysis after the pH was adjusted to 2-3 with sulfuric acid. From Figure **1**, we can see that the produced main ^{13}C compound was H^{13}COOH at 165 ppm, and this result suggests that produced formate was indeed from transfer hydrogenation of CO_2 rather than from decarboxylation of C3 compounds.

3.2. ^{1}H-NMR, ^{2}H-NMR Analyses on Hydrogen-Transfer Reduction of CO_2 into Formate with Glycerine by Alkaline Hydrothermal Reaction

To examine the solvent isotope effect on hydrogen-transfer reduction of CO_2 into formate with glycerine by alkaline hydrothermal reaction, a set of parallel experiments was performed with 0.44 g CO_2 by using 0.41 g NaOD in D_2O instead of 0.40 g NaOH in H_2O. After reaction, collected liquid samples were analyzed

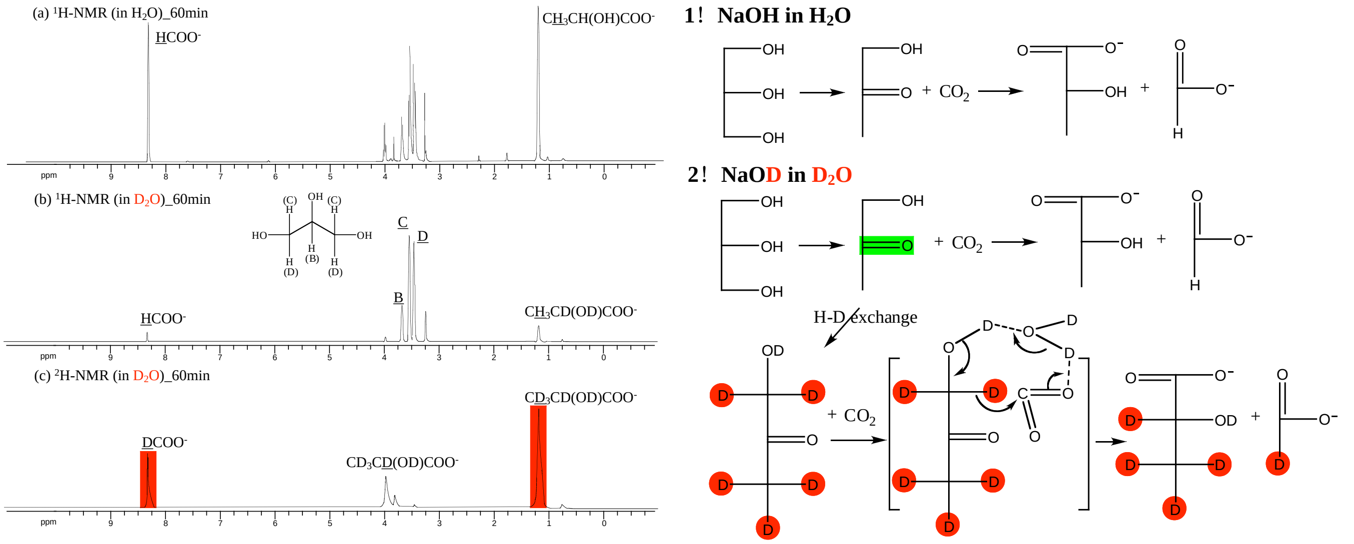

Figure 2: Spectra and scheme of collected liquid samples after the hydrothermal reactions of 0.44g CO_2 and 0.33 M glycerine at 300 °C for 30 min (**a**) ^{1}H-NMR with 0.40g NaOH in H_2O, and (**b**) ^{1}H-NMR and (**c**) ^{2}H-NMR with 0.41g NaOD in D_2O.

by the ^{1}H and ^{2}H-NMRs. In order to understand the solvent isotope of produced lactate, we first investigate the H-D exchange of lactic acid in D_2O by alkaline hydrothermal reaction. According to what reported by Kuhlmann *et al*. [7, 8], only $CH_3CD(OD)COO^-$ can be detected from $CH_3CH(OH)COO^-$ by D_2O alkaline hydrothermal reaction. In short, only α-C of carboxyl groups undergoes rapid and nearly complete H-D exchange reactions rather than simple alcohols. From spectrum (a) and (b) to (c) in Figure **2**, we can see that Ds on the β-C of produced lactate were observed undergoing H-D exchange reaction by using D_2O solvent instead of H_2O, in addition to remaining glycerine as a simple three-carbon alcohol. From these results, we can speculate that there is a ketone carbonyl group as intermediate product formed on hydrogen-transfer reduction of CO_2 into formate with glycerine by alkaline hydrothermal reaction.

3.3. LC-MS Analyses on Hydrogen-Transfer Reduction of CO_2 into Formate with Glycerine by Alkaline Hydrothermal Reaction

To order to further understand the deuterium behavior on hydrogen-transfer reduction of CO_2 into formate with glycerine by alkaline hydrothermal reaction, we analyzed the same liquid samples by LC-MS from a set of parallel experiments was performed using 0.41 g NaOD in D_2O and 0.40 g NaOH in H_2O in Figure **2**. By comparing (a1) and (b1) in Figure **3**, it can be seen that the m/z of lactate in H_2O was 89.80, but the m/z of lactate in D_2O added into 91.80, 92.85, and 93.75. This results shows that 2-4 Hs has been transformed into D of lactate in D_2O by H-D exchange reaction, and the result from LC-MS analysis shows that the α-C of carboxyl groups in produced lactate undergoes rapid and nearly complete H-D exchange in D_2O in consist with the H-NMR.

By comparing the postulated mechanisms shown in H_2O and in D_2O of Figure **2**, we can see that acetol as an intermediate product, was transformed into CD_3COCD_2OD owing to H-D exchange reaction in D_2O hydrothermal reaction. At the same time, it was confirmed that $HCOO^-$ do not participate in the H-D exchanges because $DCOO^-$ cannot be detected in D_2O experiment of formic acid under solely alkaline hydrothermal conditions. So, it can be assumed that produced formate is almost $DCOO^-$. From comparing the spectrums in Figure **2a**, **b** to **c** by H-NMR analyses and in Figure **3a2** and **b2** by LC-MS analyses, we can see that Ds of formate in D_2O experiment have almost instead of Hs of formate in H_2O, and m/z of formate in D_2O increased into 46.80. A large amount of D in formed formate and lactate not only shows that the H_2O acted as a reactant, but also shows that acetol was the most probable intermediate in the first reaction by undergoing a dehydration rather than a dehydrogenation.

4. CONCLUSION

In summary, the results from solvent isotope studies on hydrogen-transfer reduction of CO_2 into formate with

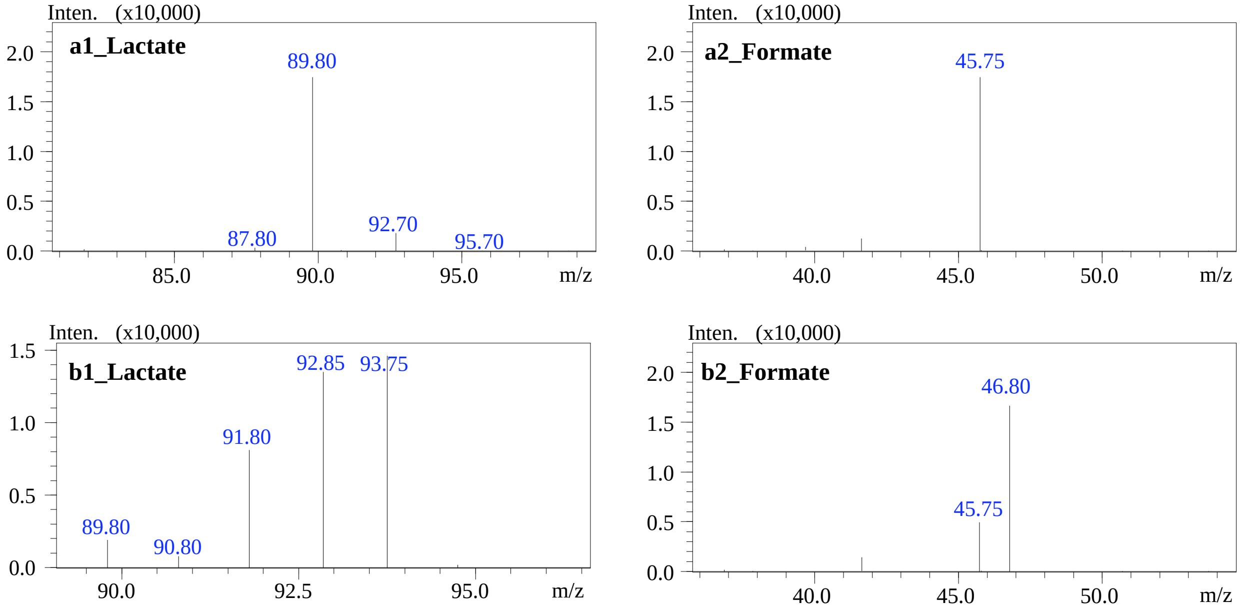

Figure 3: MS spectra of collected liquid samples after the hydrothermal reactions of 0.44g CO_2 and 0.33 M glycerine at 300 ºC for 30 min (**a**) 0.40g NaOH a in H_2O and (**b**) 0.41g NaOD in D_2O.

glycerine by alkaline hydrothermal reaction showed that (1) the observation of $H^{13}COO^-$ produced at 165 ppm suggests that abiogenic formate was indeed produced from CO_2; (2) H-D exchanges on the β-C of lactate by D_2O hydrothermal reaction suggests that a ketone carbonyl group as intermediate product was formed on hydrogen-transfer reduction of CO_2 into formate with glycerine by alkaline hydrothermal reaction; (3) A large amount of D in formed formate and lactate not only shows that the H_2O acted as a reactant, but also shows that acetol was the most probable intermediate in the first reaction by undergoing a dehydration rather than a dehydrogenation.

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