

# Solvent Isotope Effect on Transfer Hydrogenation of H<sub>2</sub>O with Glycerine under Alkaline Hydrothermal Conditions

Zheng Shen<sup>\*</sup>, Minyan Gu, Shiyang Liu, Wenjie Dong and Yalei Zhang

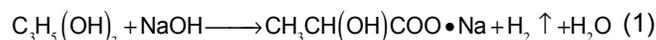
National Engineering Research Center of Facilities Agriculture, State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai 200092, China

**Abstract:** Solvent isotope effect was investigated with <sup>1</sup>H-, <sup>2</sup>H-NMR, LC-MS and Gas-MS analyses on transfer hydrogenation of H<sub>2</sub>O with glycerine under alkaline hydrothermal conditions. The results from solvent isotope studies showed that (1) the H on the β-C of lactate was almost exchanged by D<sub>2</sub>O, which suggests that the hydroxyl (-OH) group on the 2-C of glycerine was first transformed into a carbonyl (C=O) group and then was converted back into a -OH group to form lactate; (2) The presence of large amounts of D was found in the produced hydrogen gas, which shows that the water molecules acted as a reactant; and (3) D% in the produced hydrogen gas was far more than 50%, which straightforwardly shows that acetol was formed in the first place as the most probable intermediate by undergoing a dehydration reaction rather than a dehydrogenation reaction.

**Keywords:** Solvent isotope effect, transfer hydrogenation, glycerine, hydrothermal reaction.

## 1. INTRODUCTION

Glycerine has been attracted attention as a potentially important biorefinery feedstock, and as a by-product of the transesterification of plant oils and animal fats, its availability could potentially increase with the expected increase in biodiesel production [1-2]. Glycerine is commonly regarded as a waste product of transesterification; however, it has many applications that could add value to the entire process. For instance, researchers have reported that glycerine has the potential to be converted into some important commodity chemicals using novel methods [3-4]. Furthermore, in our previous study, we found that on transfer hydrogenation of H<sub>2</sub>O with glycerine, glycerine could be effectively converted into lactate under alkaline hydrothermal conditions and that the molar yield of hydrogen was almost equal to that of lactate (Eqs. 1) [5]. Lactate is an important material because it is used for producing biodegradable lactic acid polymers and is an important chemical feedstock as a synthetic precursor. Recently, although many researchers suggested that the first step on the conversion of glycerine into lactate is a dehydrogenation reaction rather than a dehydration reaction, any direct and objective evidence regarding the mechanism was not provided [6-8]. To discover the reaction mechanism for the production of lactate from glycerine under alkaline hydrothermal conditions, we investigated the solvent isotope effect on transfer hydrogenation of H<sub>2</sub>O by glycerine with <sup>1</sup>H-, <sup>2</sup>H-NMR, LC-MS and Gas-MS analyses.



## 2. EXPERIMENTAL PROCEDURE

A mixture of 2 mL of 0.66 M glycerine (99%) and 2 mL of 2.5 M NaOH (or NaOD) in H<sub>2</sub>O (or D<sub>2</sub>O, 99.9% D) were poured into a batch-type reactor, which was made of a stainless steel SUS 316 tube (3/8 inch diameter, 1-mm wall thickness, 120-mm length) with two-end fittings, providing an inner volume of 5.7 mL. 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 <sup>1</sup>H, the amount of <sup>1</sup>H 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. The reactor was placed into a salt bath preheated to a desired temperature. In the salt bath, the reactor was shaken horizontally to enable proper mixing and enhanced heat transfer. After the desired reaction time, the reactor was removed from the salt bath and placed 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. Overall, the real reaction time was shorter than the apparent reaction time because the heating time of the reaction media from 20 to 300 °C was approximately 15 s. The temperature of the salt bath was taken as the reaction temperature. In all of experiments, deionized water was used, and the reactor was purged with nitrogen to remove any dissolved oxygen prior to the reactions. After cooling, samples from the liquid phase in the reactor were collected for analysis by <sup>1</sup>H-, <sup>2</sup>H-NMRs using an NMR

<sup>\*</sup>Address correspondence to this author at the National Engineering Research Center of Facilities Agriculture, State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai 200092, China; Tel/Fax: 86-21-65985811; E-mail: shenzheng@tongji.edu.cn

spectrometer (DMX 500, 500 MHz) and by LC-MS (Shimadzu 2010A). A mass spectrometer was used an electro-spray ionization (ESI) apparatus in negative mode, and the LC conditions were as follows: mobile phase, 0.1% aqueous formic acid; flow rate, 0.25 mL/min; detection, UV 210 nm; and temperature, 50 °C. Samples from the gas phase in the reactor were collected for analysis by Gas-MS (Thermo-Finnigan MAT 271).

### 3. RESULTS AND DISCUSSION

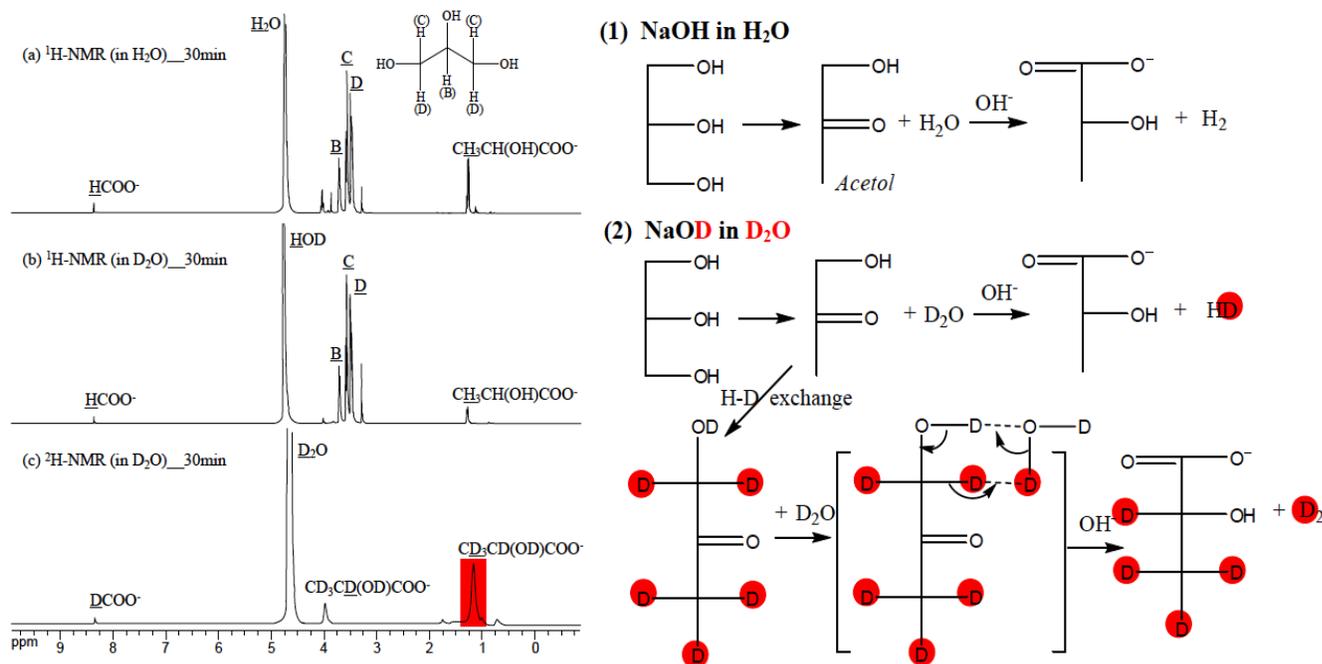
#### 3.1. <sup>1</sup>H- and <sup>2</sup>H-NMR Analyses on Transfer Hydrogenation of H<sub>2</sub>O with Glycerine Under Alkaline Hydrothermal Conditions

To investigate the solvent isotope effect, a deuterium transformation study was performed using D<sub>2</sub>O, and the results are displayed in the <sup>1</sup>H- and <sup>2</sup>H-NMRs in Figure 1. In an independent run, we confirmed that CH<sub>3</sub>CH(OH)COO<sup>-</sup> can be only transformed into CH<sub>3</sub>CD(OD)COO<sup>-</sup> rather than into CD<sub>3</sub>CD(OD)COO<sup>-</sup> in D<sub>2</sub>O under the alkaline hydrothermal conditions. Interestingly, Kuhlmann *et al.* also investigated the behaviours of several different organic compounds in subcritical D<sub>2</sub>O to determine the kinetics of H/D exchange, and they found that simple alcohols do not participate in H/D exchange reactions, whereas the α positions of ketone carbonyl groups (e.g., the CH<sub>3</sub> groups of acetone) undergo rapid and nearly complete

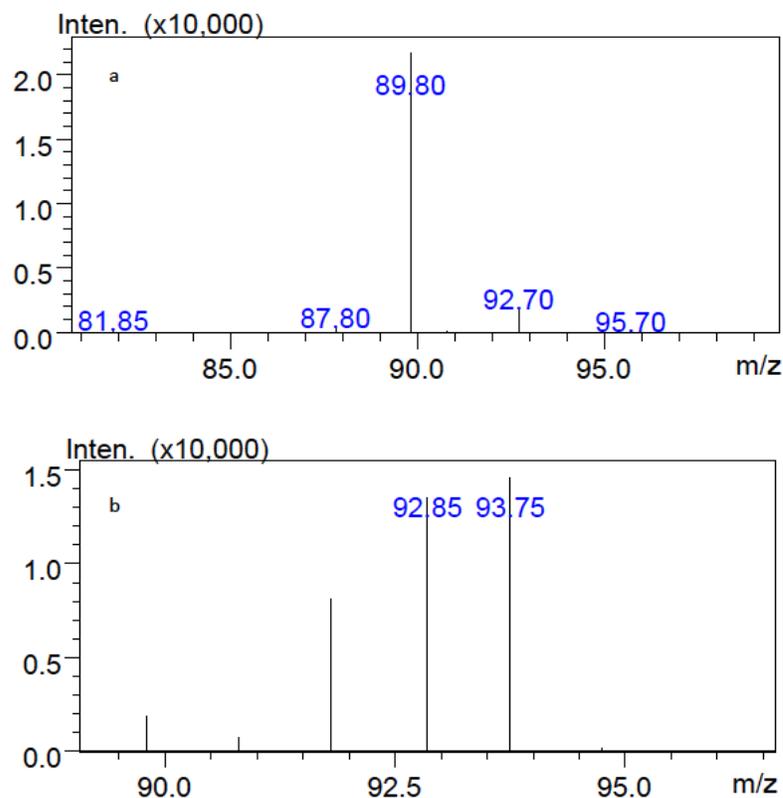
exchange [9-10]. By comparing spectrum (a) and (b) to (c) in Figure 1, it can be observed that the H on the β-C of lactate has been almost transformed into D when in D<sub>2</sub>O, and remaining glycerine do not take place H/D exchange reaction. This result indicates that there is an intermediate product including a ketone carbonyl group, such as R<sub>1</sub>-CO-R<sub>2</sub>, formed during the production of lactate from glycerine because of the H/D exchange on the β-C of lactate.

#### 3.2. LC-MS Analyses on Transfer Hydrogenation of H<sub>2</sub>O with Glycerine Under Alkaline Hydrothermal Conditions

To further understand the deuterium behavior in the formation of lactate from glycerine in D<sub>2</sub>O under alkaline hydrothermal conditions, the liquid samples obtained from the reaction of glycerine and NaOD at a temperature of 300 °C were also analyzed by LC-MS. As shown in Figure 2a and b, the m/z of lactic acid after reacting in H<sub>2</sub>O was 89.80, but the m/z of lactic acid after reacting in D<sub>2</sub>O increased to 91.75, 92.85, and 93.75. This result from the LC-MS analysis is consistent with that of the previous H-NMR analysis, where a large number of Hs on the β-Cs of lactic acid were indeed exchanged by D in D<sub>2</sub>O. Furthermore, 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 lactic acid.



**Figure 1:** Spectra and scheme for the solution after the hydrothermal reaction of 0.33 M glycerine at 300 °C for 30 min (a) <sup>1</sup>H-NMR with 1.25 M NaOH in H<sub>2</sub>O, and (b) <sup>1</sup>H-NMR and (c) <sup>2</sup>H-NMR spectra with 1.25 M NaOD in D<sub>2</sub>O.



**Figure 2:** MS spectra of the lactic acid solutions after the hydrothermal reactions of 0.33 M glycerine at 300 °C with (a) 1.25 M NaOH in H<sub>2</sub>O and (b) 1.25 M NaOD in D<sub>2</sub>O.

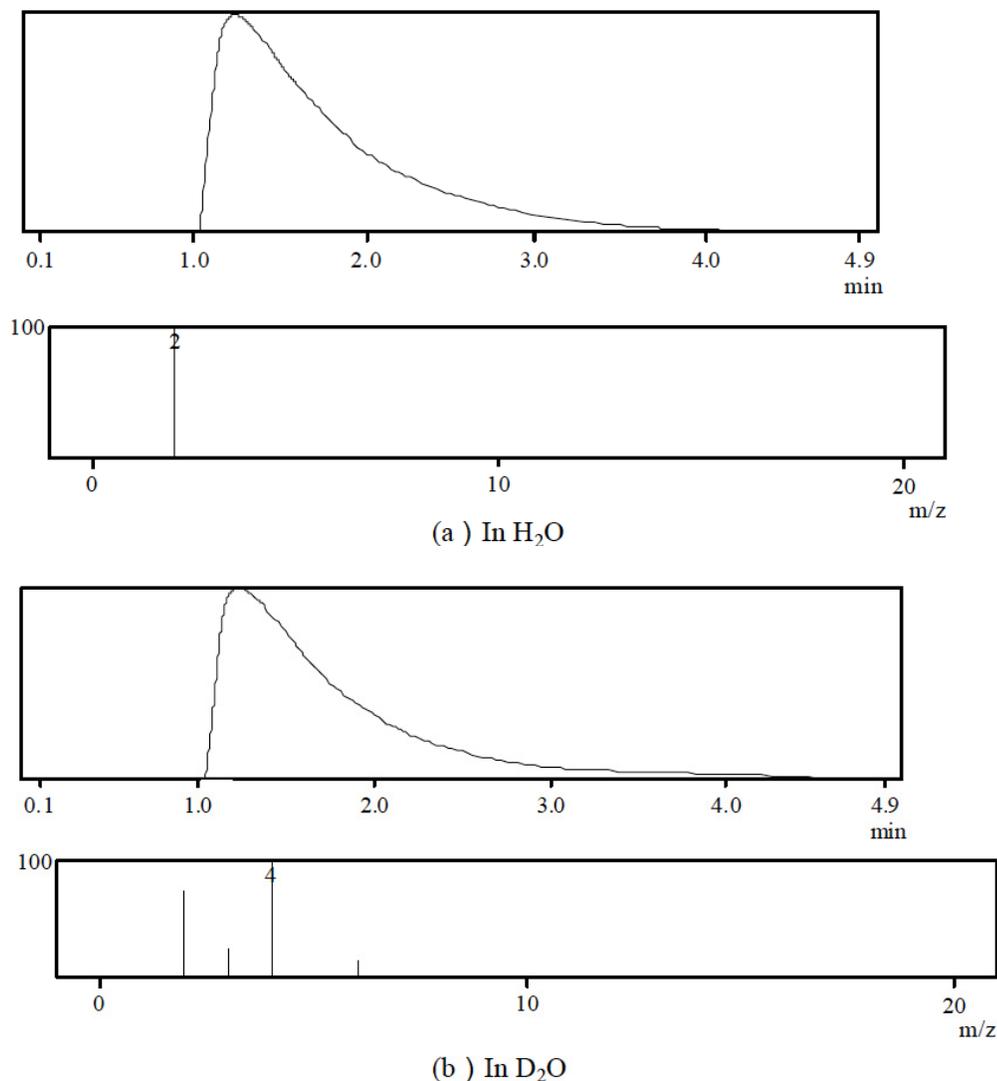
### 3.3. Gas-MS Analyses on Transfer Hydrogenation of H<sub>2</sub>O with Glycerine Under Alkaline Hydrothermal Conditions

From the postulated mechanism shown in Scheme (1) and (2) of Figure 1, H in OH-C of acetol took place H/D exchange reaction in D<sub>2</sub>O hydrothermal conditions, similar to H in β-C of acetol. Arita *et al.* reported that hydrogen can be generated by an ethanol oxidation reaction catalyzed by water molecules and that half of the produced hydrogen can come from the water in accordance with the proposed reaction mechanism [11]. Moreover, Takahashi *et al.* suggested that water molecules play significant catalytic roles in ethanol oxidation reactions based on ab initio density functional theory calculations [12-13]. In an independent run, we confirmed that H<sub>2</sub> cannot be transformed into HD or D<sub>2</sub> in D<sub>2</sub>O under solely alkaline hydrothermal conditions. From the above, we can predict that in D<sub>2</sub>O reactions, the D% in the produced hydrogen would be greater than 50%. So, in order to determine the proportion of D in the produced hydrogen, the gas samples obtained from the reaction of glycerine with NaOH in H<sub>2</sub>O and with NaOD in D<sub>2</sub>O at a temperature of 300 °C were analyzed by Gas-MS. Figure 3 shows the gas chromatograms and MS spectra of the gases after the

hydrothermal reactions of glycerine at 300 °C with NaOH in H<sub>2</sub>O and NaOD in D<sub>2</sub>O. The results showed that the hydrogen ratios of D<sub>2</sub>, HD, and H<sub>2</sub> were respectively 70%, 25%, and 5% after the reaction of glycerine with NaOD in D<sub>2</sub>O. The presence of large amounts of D in the produced hydrogen gas shows that the water molecules acted as a reactant. More importantly, D% of far more than 50% straightforwardly showed that acetol was formed in the first place as the most probable intermediate by undergoing a dehydration reaction and a keto-enol tautomerization reaction. This is because that if the dehydrogenation reaction is a first step<sup>4</sup>, only D ratio of generated hydrogen is 50%. Regardless of the first occurrence of the dehydrogenation reaction or dehydration reaction, pyruvaldehyde formed in both postulated mechanisms can also explain H/D exchanges in α-C and β-C of lactic acid.

### 4. CONCLUSION

In summary, the results from solvent isotope studies showed that (1) the H on the β-C of lactate was almost exchanged by D<sub>2</sub>O, which suggests that the hydroxyl (-OH) group on the 2-C of glycerine was first transformed into a carbonyl (C=O) group and then was converted



**Figure 3:** Gas chromatograms and MS spectra for the gas samples after the hydrothermal reactions of 0.33 M glycerine at 300 °C with (a) 1.25 M NaOH in H<sub>2</sub>O and (b) 1.25 M NaOD in D<sub>2</sub>O.

back into a -OH group to form lactate; (2) The presence of large amounts D was found in the produced hydrogen gas, which shows that the water molecules acted as a reactant; and (3) D% in the produced hydrogen gas was far more than 50%, which straightforwardly shows that acetol was formed in the first place as the most probable intermediate by undergoing a dehydration reaction rather than a dehydrogenation reaction.

#### ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial supports provided by the National Natural Science Foundation of China (No. 21376180), the National High Technology Research and Development Program of China (863 Program) (No. 2013AA103006), the Fundamental Research Funds for the Central

Universities (No. 2870219021) and Project of Shanghai Science and Technology Commission of China (No. 12231205202).

#### REFERENCES

- [1] Cardone M, Mazzoncini M, Menini S, Rocco V, Senatore A, Seggiani M, Vitolo S. Brassica carinata as an alternative oil crop for the production of biodiesel in Italy: agronomic evaluation, fuel production by transesterification and characterization. *Biomass Bioenerg* 2003; 25: 623-36. [http://dx.doi.org/10.1016/S0961-9534\(03\)00058-8](http://dx.doi.org/10.1016/S0961-9534(03)00058-8)
- [2] Cerce T, Peter S, Weidner E. Biodiesel transesterification of biological oils with liquid catalysts: Thermodynamic properties of oil-methanol-amine mixtures. *Ind Eng Chem Res* 2005; 44: 9535-41. <http://dx.doi.org/10.1021/ie050252e>
- [3] Behr A, Eilting J, Irawadi K, Leschinski J, Lindner F. Improved utilisation of renewable resources: New important derivatives of glycerol. *Green Chem* 2008; 10: 13-30. <http://dx.doi.org/10.1039/B710561D>

- [4] Zhou CH, Beltramini JN, Fan YX, Lu GQ. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem Soc Rev* 2008; 37: 527-49.  
<http://dx.doi.org/10.1039/B707343G>
- [5] Kishida H, Jin F, Zhou Z, Moriya T, Enomoto H. Conversion of Glycerin into Lactic Acid by Alkaline Hydrothermal Reaction. *Chem Lett* 2005; 34:1560-61.  
<http://dx.doi.org/10.1246/cl.2005.1560>
- [6] Auneau F, Miche C, Delbecq F, Pine C, Sautet P. Unravelling the Mechanism of Glycerol Hydrogenolysis over Rhodium Catalyst through Combined Experimental-Theoretical Investigations. *Chem Eur J* 2011; 17: 14288-99.  
<http://dx.doi.org/10.1002/chem.201101318>
- [7] Roy D, Subramaniam B, Chaudhar RV. Cu-Based Catalysts Show Low Temperature Activity for Glycerol Conversion to Lactic Acid. *ACS Catal* 2011; 1: 548-51.  
<http://dx.doi.org/10.1021/cs200080j>
- [8] Ramírez-López CA, Ochoa-Gómez JR, Fernández-Santos M, Gómez-Jiménez-Aberasturi O, Alonso-Vicario A, Torrecilla-Soria J. Synthesis of lactic acid by alkaline hydrothermal conversion of glycerol at high glycerol concentration. *Ind Eng Chem Res* 2010; 49: 6270-78.  
<http://dx.doi.org/10.1016/j.biortech.2011.04.007>
- [9] Kuhlmann B, Arnett EM, Siskin M. Classical Organic Reactions in Pure Superheated Water. *J Org Chem* 1994; 59: 3098-101.  
<http://dx.doi.org/10.1021/jo00090a030>
- [10] Kuhlmann B, Arnett EM, Siskin MJ. H-D Exchange in Pinacolone by Deuterium Oxide at High Temperature and Pressure. *Org Chem* 1994; 59: 5377-80.  
<http://dx.doi.org/10.1021/jo00097a046>
- [11] Takahashi H, Hisaoka S, Nitta T. Ethanol Oxidation Reactions Catalyzed by Water Molecules:  $\text{CH}_3\text{CH}_2\text{OH} + n\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2 + \text{H}_2\text{O}$  ( $n=0,1,2$ ). *Chem Phys Lett* 2002; 363: 80-6.  
[http://dx.doi.org/10.1016/S0009-2614\(02\)01142-9](http://dx.doi.org/10.1016/S0009-2614(02)01142-9)
- [12] Arita T, Nakahara K, Nagami K, Kajimoto O. Hydrogen generation from ethanol in supercritical water without catalyst. *Tetrahedron Lett* 2003; 44: 1083-86.  
[http://dx.doi.org/10.1016/S0040-4039\(02\)02704-1](http://dx.doi.org/10.1016/S0040-4039(02)02704-1)
- [13] Takahashi H, Hashimoto H, Nitta T. Quantum mechanical/molecular mechanical studies of a novel reaction catalyzed by proton transfers in ambient and supercritical states of water. *J Chem Phys* 2003; 119: 7964-71.  
<http://dx.doi.org/10.1063/1.1610440>

Received on 22-04-2014

Accepted on 06-05-2014

Published on 30-05-2014

DOI: <http://dx.doi.org/10.6000/1929-6002.2014.03.02.5>