



Production of formic acid from CO₂ reduction by means of potassium borohydride at ambient conditions



Cameron Fletcher^a, Yijiao Jiang^{b,*}, Rose Amal^{a,*}

^a School of Chemical Engineering, UNSW Australia, Sydney, NSW 2052, Australia

^b Department of Engineering, Macquarie University, Sydney, NSW 2109, Australia

HIGHLIGHTS

- High-yield production of formic acid by reduction of CO₂ at ambient conditions.
- 0.15 mol/L of formic acid were produced by using 0.5 M borohydride solution.
- Time-resolved *in situ* NMR was firstly developed to understand the process.
- A reaction mechanism involved in CO₂ reduction and BH₄⁻ hydrolysis was established.

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ABSTRACT

The present study provides an efficient process for the high-yield production of formic acid (24%) by reduction of carbon dioxide (CO₂) with potassium borohydride at ambient conditions. The effects of reaction temperature, CO₂ pressure and borohydride concentration have been investigated. For a 0.5 M borohydride solution, 0.15 mol/L of formic acid were produced at room temperature and ambient pressure with yields increasing at higher pressures. A time-resolved *in situ* ¹H and ¹¹B nuclear magnetic resonance (NMR) technique was firstly developed to monitor the elementary reaction processes under real working conditions. Direct evidence is given for the formation of H₂, HD and a hydroxyborohydride intermediate (BH₃OH⁻) formed during borohydride decomposition indicating that the source of the hydrogen gas comes from both the borohydride anion and water, while borohydride works as a water-splitting reagent. Consequently, a reaction mechanism involved in both borohydride hydrolysis and CO₂ reduction has been established.

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1. Introduction

With the increasing socio-political pressure on reducing carbon dioxide (CO₂) emissions, CO₂ is becoming a promising carbon source with a zero or even negative cost and practically unlimited availability for the sustainable chemical manufacturing of hydrocarbon fuels and their derivatives (Centi et al., 2011; Quadrelli and Centi, 2011). CO₂ itself has the advantages of being nontoxic, abundant, and an economical chemical reagent (Sakakura et al., 2007). Reduction of CO₂ can lead to various compounds such as formic acid, acetic acid, formaldehyde, methanol, CO, and CH₄, etc. Among these products, formic acid and methanol hold a central position because they are both important feedstock for the manufacture of everyday chemicals. However, since CO₂ is

thermodynamically one of the most stable commonly encountered carbon-bearing molecules, a large energy input and/or a high energy substrate such as hydrogen (H₂) is required to reduce CO₂ into useful chemicals (Centi and Perathoner, 2009). Conventional hydrogenation of CO₂ to hydrocarbon products generally requires high energy inputs and is thus performed at elevated temperatures and/or under immense pressures of up to 950 atm (Tidona et al., 2013). This severely limits the utility of such reactions due to the high energy and equipment costs. Additional difficulties occur due to the storage and subsequent handling of gaseous H₂ at high temperatures and pressures as a result of stringent safety measures that must be adhered to.

Borohydrides (BH₄⁻) are an alternative high energy carrying substrate with some of the highest gravimetric hydrogen densities. They have provided an exceptional tool for chemists and enable the facile reduction of organic molecules in a wide variety of systems (Brown and Krishnamurthy, 1979). More recently there has been a vast amount of interest in borohydride salts as hydrogen storage materials due to their high volumetric and

* Corresponding authors. Tel.: +612 9385 4361; fax: +612 9385 5966.

E-mail addresses: yijiao.jiang@mq.edu.au (Y. Jiang), r.amal@unsw.edu.au (R. Amal).

gravimetric hydrogen capacities, as well as the unique fact that when coupled with water the evolved hydrogen originates from both the borohydride and water. As indicated by the stoichiometry of the Equation ($\text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow \text{BO}_2^- + 4\text{H}_2$), half of the H_2 produced in the hydrolysis reaction is theoretically derived from the solution water which accounts for the unusually large amount of H_2 generated in this reaction (Dovgaliuk et al., 2014a, 2014b). It is important to balance the stability of the solution with the ease at which hydrogen can be released. Compared to lithium and sodium borohydrides, potassium borohydride (KBH_4) exhibits much slower self-hydrolysis when in contact with water without the aid of any promoters (Liu and Li, 2009; Sahin et al., 2007). This stability makes KBH_4 an excellent hydrogen storage material as the generation of hydrogen can be turned on or off with the addition of a suitable promoter (Dovgaliuk et al., 2014a, 2014b).

It has been proposed that the mechanism for borohydride hydrolysis proceeds through the formation of an initially slow forming hydroxyborohydride species (BH_3OH^-) intermediate, which rapidly decomposes through the addition of subsequent hydroxyl groups and the release of hydrogen. Due to the transitory nature of this BH_3OH^- species, it is normally only faintly observed, if at all, and as a consequence its reducing properties are relatively unknown. Of the few studies available (Molina Concha et al., 2011; Reed and Jolly, 1977; Ruman et al., 2007; Sanli et al., 2011; Santos and Sequeira, 2010), there are conflicting reports as to the reducing power of this species and as such further insight is greatly needed. While much research has already been devoted to hydrogen generation through borohydride hydrolysis, it is still somewhat doubtful if the reduction rate of CO_2 by the produced H_2 from borohydride hydrolysis is sufficiently high to produce high yield of formic acid and methanol. The understanding of borohydride hydrolysis and the reduction mechanism of CO_2 is of great importance for an effective system design.

As an alternative using gaseous H_2 as a reducing agent, we herein report a simple one-pot high-yielding ambient process for CO_2 reduction to produce formic acid by reaction with aqueous potassium borohydride. The effects of changing borohydride concentration and CO_2 pressure were examined. Unlike hydrogenation of CO_2 under harsh temperature and/or pressurized conditions, this process shows incredible promise by proceeding spontaneously at room temperature and ambient pressure. This greatly reduces the complexity and cost of the necessary operating equipment. To understand in detail the process by which CO_2 can be selectively reduced to formic acid, a time-resolved *in situ* ^1H and ^{11}B NMR technique was first developed to study the reaction process under real working condition. Based on the experimental results, a reasonable reaction mechanism of formic acid formation from borohydride hydrolysis and CO_2 reduction is presented in this work.

2. Experimental

2.1. Reduction of CO_2 by means of potassium borohydride

Potassium borohydride was dissolved in water immediately prior to all reactions to prevent potential decomposition by hydrolysis. For the kinetic and borohydride concentration studies CO_2 was bubbled continuously into the reaction mixture to ensure that the solution was saturated at all times throughout the reaction. In the case of high-pressure reactions borohydride solution was placed in a 300 ml Parr pressure vessel and pressurized to the desired level with CO_2 . The reaction mixture was stirred continuously at this pressure for 1.5 h before being depressurized and analyzed. Formic acid concentration was quantified by high performance liquid chromatography (HPLC) using a Waters

Alliance 2695 Separations Module coupled with a Waters 410 Differential Refractometer (RI). Separation was performed on an Aminex HPX-87H Ion Exclusion Column at 40 °C with a flow-rate of 6.0 ml/min of 5 mmol/l sulfuric acid.

2.2. *In situ* NMR experiments

The *in situ* NMR experiments were performed at room temperature on both 300 and 600 MHz instruments. For the 300 MHz measurements, a Bruker DPX III 300 MHz spectrometer equipped with a 5 mm BBFO Z-gradient broadband probe was utilized. The instrument was operated at 300.3 MHz for ^1H and 96.4 MHz for ^{11}B , respectively. The chemical shifts of ^1H and ^{11}B were referenced to tetramethylsilane (TMS) and boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$), respectively. A 90° pulse width of 14.9 μs (at a transmission power of 2.5 dB) for ^1H and 9.53 μs (transmission power –1.00 dB) for ^{11}B were used, respectively. ^1H measurements were acquired after 16 scans at a resolution of 65 K leading to a digital resolution of 0.091 Hz/point. ^{11}B measurements were acquired after 128 scans with 65 K data points resulting in a digital resolution of 0.24 Hz/point. For ^1H measurements an acquisition time of 5.55 s and delay of 1 s was used and for ^{11}B measurements a 2.15 s acquisition time and 0.3 s delay was used. For the 600 MHz measurements, a Bruker Avance III 600 MHz spectrometer equipped with a 5 mm BBFO Plus Z-gradient broadband probe was used. The instrument was operated at 600.1 MHz for ^1H measurements. An exponential window function with a line broadening parameter of 0.3 Hz was applied to the raw free induction decay (FID) data to improve the signal to noise ratio in the final spectra.

Potassium borohydride was dissolved in deuterium oxide (D_2O) immediately prior to the NMR analysis to form 1 ml of a 0.5 mol/L solution. The solution was inserted into a modified NMR tube featuring a sealable lid and septum, as depicted in Fig. 1. Two low pressure gas lines entered the NMR tube through the septum, one reaching down to ~ 1 mm above the probe height and the second resting just below the septum as a vent to prevent pressure build-up within the tube. The first line was connected to a portable pressure vessel filled with CO_2 at a pressure of 15 bar via a regulating valve and a needle valve so that the gas flow rate could be controlled. At the commencement of the experiment a short burst of CO_2 was bubbled into the tube after which the gas flow

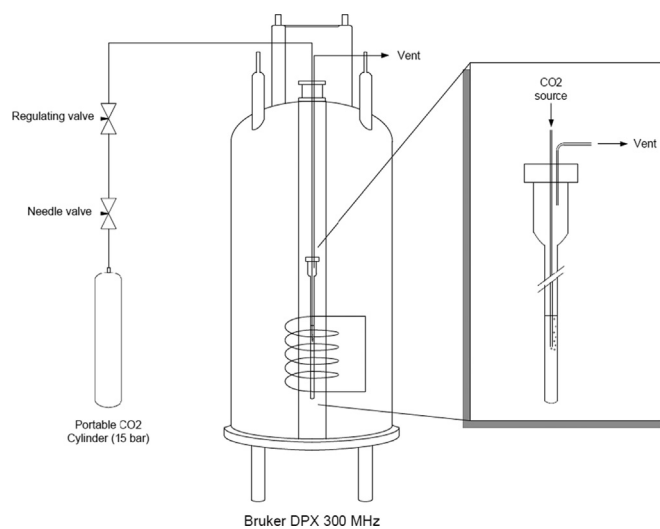


Fig. 1. Diagram of the apparatus used for the time-resolved *in situ* NMR measurements for the study of CO_2 reduction by means of aqueous potassium borohydride. A custom-made NMR tube was inserted in the NMR probe as shown in the insert on the right.

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