



Conversion of Carbon Dioxide from Air to Methanol, Formaldehyde, Formic Acid and Ammonium Pentaborate Tetrahydrate

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Abstract: A process for sequestering CO₂ from air by sparging air through an NH₄OH solution and adding NaBH₄ produces formic acid, formaldehyde, methanol and ammonium pentaborate tetrahydrate in appreciable yields. This sparging chemistry centers around the well-known phenomenon of carbonate in strong bases. The newly discovered chemistry is based on H⁻ as a nucleophile that can attack a nucleofuge, the carbonyl in carbonate in strong base. NaHCO₃ was used as a positive control for the sparging method giving nearly identical IR spectra for sparged NH₄OH and, NaHCO₃ added NH₄OH. This novel chemistry can be shown to produce H⁻ substitution products of sulfate and phosphate esters of carbohydrates. The H⁻ nucleophile adds one, two and three H atoms to carbonate, for formic acid, formaldehyde and methanol, respectively, two H atoms to sulfate esters and one H atom to phosphate. In this way phosphate versus sulfate substitution can be discerned by mass spectrometry using this chemistry. The pH profile of the reaction mixture for the NaHCO₃ dissolved in 1 N NH₄OH first dropped below starting pH possibly because the reaction vessel was capped, allowing NH₃(g) to evolve and possibly drive the reaction forward. But then the pH returned to a slight lower pH than the starting pH 11.4. This novel chemistry may allow a sustainable reduction in the green-house gas, CO₂, worldwide, to relieve pressure on food uses for corn and thereby avert food shortages throughout the world.

Keywords: Sequestration by Sparging Air, Conversion of CO₂, Formic Acid, Methanol, Formaldehyde, Ammonium Pentaborate Tetrahydrate

1. Introduction

CO₂, a green-house gas, is debated to cause climate change in the world, that is, an increase in global temperature with consequences that could cause food prices to go up and cause food shortages in the third world. A process to produce formic acid from air using lithium aluminum hydride has been attempted in the gas phase. [1] A NaBH₄ and Na₂CO₃ system to reduce aldehydes and ketone has been published but, presumably carbonate, was not reduced because it was done in aqueous solution without excess NH₄OH in solution. [2] A process to reduce CO₂ to methanol using a carbene catalyst was published. [2] Hydrogenation of NaHCO₃ to methanol has been reported. [2] These processes, with references to this work are

contained in a patent that is based on the work presented here, has been published. [2] A method for the discernment of sulfate and phosphate esters of carbohydrate esters has been reported. [3] This chemistry involves the nucleophilic attack of H⁻ on sulfonyl, S=O, and phosphoryl, P=O, groups that are esterified to carbohydrates. The attack is on the heteroatom which has developed a partial positive charge, attracting the nucleophile. This is novel chemistry. The sulfate ester adds two hydrogen atoms and the phosphate ester adds one hydrogen atom and this difference, with the difference between the atomic mass of sulfur and phosphorous gives a total difference of 2.0 amu in the mass spectrometer. Underivatized sulfate and phosphate are isobaric in the mass spectrometer. Applications of this chemistry are found for treatment of malaria virus with a

kappa casein product obtained by reaction of this glycoprotein with NaBH_4 in NH_4OH . [4] This chemistry was also applied to the preparation of a 1,5 anhydro sialyl lactose phosphate for identification purposes to assist in giving credence to the presence of the oligosaccharide di-phospho asparaginy sulfo tyrosine dipeptide found in bovine milk. It may allow the use of bovine milk for the treatment of leprosy. [5] This chemistry has been applied to the reaction of neo-kestose 1,6 di-phosphate, in NaBH_4 in NH_4OH , to a possible inhibitor of fructose 1,6 bisphosphate aldolase, a well-known cancer target. [6] Also, this chemistry has been applied to prepare a sulfo derivative of 1,5 anhydro L-fucitol as a possible P selectin blocker. [7] Other applications of this chemistry are noted. [8-9] For an in depth treatise on Boron Hydride chemistry note the work edited by Muetterties [10]. The most recent chemistry that may be related is found in Wang and Yu. [11] Other work has been done to reduce carbon dioxide to valuable chemicals. [12-15]

Applying this reaction, NaBH_4 in aqueous NH_4OH , CO_2 sequestration by sparged air through this solution, is converted to valuable chemicals; formic acid, formaldehyde, methanol and ammonium pentaborate tetrahydrate. A process for this reaction is described below.

3. Results and Discussion

Table 1. IR Spectral Absorptions and Assignments.

CH₃OH Standard	CH₃OH from Bubbled Air-Water (Extracted with CH₂Cl₂: (CH₃)₂C=O)	CH₃OH from NaHCO₃ (Extracted with CH₂Cl₂: (CH₃)₂C=O)
640 cm ⁻¹	680 cm ⁻¹ formaldehyde 1170 cm ⁻¹ , H—C—O—H, CH ₃ OH 1210 cm ⁻¹ , H—C—C=O, (CH ₃) ₂ C=O	685 cm ⁻¹ formaldehyde 1170 cm ⁻¹ , H—C—OH, CH ₃ OH 1215 cm ⁻¹ , H—C—C=O, (CH ₃) ₂ C=O
1160 cm	1310 cm ⁻¹ , unknown 1360 cm ⁻¹ , HCO ₂ - Na ⁺ (CH ₃) ₂ C=O 1655 cm ⁻¹ , formaldehyde	1310 cm ⁻¹ , unknown 1370 cm ⁻¹ , HCO ₂ - Na ⁺ (CH ₃) ₂ C=O 1650 cm ⁻¹ , formaldehyde
2560 cm ⁻¹ –3840 cm ⁻¹ , O—H, CH ₃ OH	2900 cm ⁻¹ , formic acid 3290 cm ⁻¹ –3490 cm ⁻¹ , O—H, CH ₃ OH	2940 cm ⁻¹ , formic acid 3000 cm ⁻¹ –3570 cm ⁻¹ , O—H, CH ₃ OH

Found in table 1 are the wavenumbers, in cm⁻¹, for each IR spectrum both air sparged and NaHCO₃ reaction mixtures and compared.

Table 1 Infra-red peak identifications for CO₂ to formic acid, formaldehyde and methanol.

Peaks found are consistent with the presence of formic acid, formaldehyde and methanol. Only small differences

2. Materials and Methods

Ambient air was sparged through a solution of NH_4OH (1N, pH 11.4) containing NaBH_4 (Sigma-Aldrich Chemical Co. Saint Louis, MO USA). The reaction mixture was allowed to stand at ambient temperature. The pH was determined at various times. The reaction mixture was in a closed vessel during the reaction. This mixture was then extracted with CH_2Cl_2 (equal volume) and placed on an IR NaCl salt plate, immediately and the spectrum determined by a Beckman analog IR spectrometer. The wavenumbers of the peaks were compared to standard IR spectra.

In another reaction flask, NaHCO_3 was added to a solution with the same concentrations of NaBH_4 and NH_4OH but without sparging with ambient air. The reaction mixture was worked up, as noted above, and an IR spectrum was obtained as noted above after work-up.

After the, sparged with air, reaction was extracted the aqueous phase volume was reduced to approximately half its original volume. Crystals appeared, collected and washed with NH_4OH (1N). The crystals were dried with ambient air drying. A melting point was determined on a standard melting point apparatus.

between sparged air and NaHCO₃ for starting carbon source were observed.

Formic acid gave diagnostic peak at 2900cm⁻¹. Formaldehyde in the mixture produced a group of peaks at; 680cm⁻¹ and 1655cm⁻¹. Methanol gave a peak at 1170cm⁻¹, a sharp peak, and a broad peak at 3490cm⁻¹.

Table 2. Possible Identities of the Crystalline Solid.

Compound	Solubility	Melting Point
Ammonium formate	102g/100mL	116°C
Ammonium pentaborate tetrahydrate	10.9g/100mL	110°C – H ₂ O
Ammonium bicarbonate	11.9g/100mL	107°C
Ammonium carbonate	100g/100mL	258°C
Sodium formate	—	253°C
Sodium borate	—	75°C
Sodium bicarbonate	—	270°C – CO ₂
Sodium bicarbonate hydrate	—	100°C – H ₂ O

Table 2 Melting point and solubility for various ammonium salts.

In Table 2 are given melting points for possible solids obtained by reducing the aqueous reaction solution by

approximately one half.

The loss of liquid, presumably H_2O , at approximately 100°C , happens but white solid material still remains. The melting point apparatus was allowed to go to higher temperatures, 150°C , but no melting occurred. The loss of water came at approximately 103° to 106°C . No other molecules, published standards, were reported to produce the loss of liquid at this temperature. The values for melting

point, loss of H_2O , are reasonable and suggest that the solid produced in the reaction of carbonate with NaBH_4 in NH_4OH , aqueous, is ammonium pentaborate tetrahydrate.

A mechanism is proposed in Figure 1 for the chemistry of converted /sequestered carbon dioxide by H^- nucleophilic attack to produce formic acid, formaldehyde, methanol and ammonium pentaborate tetrahydrate.

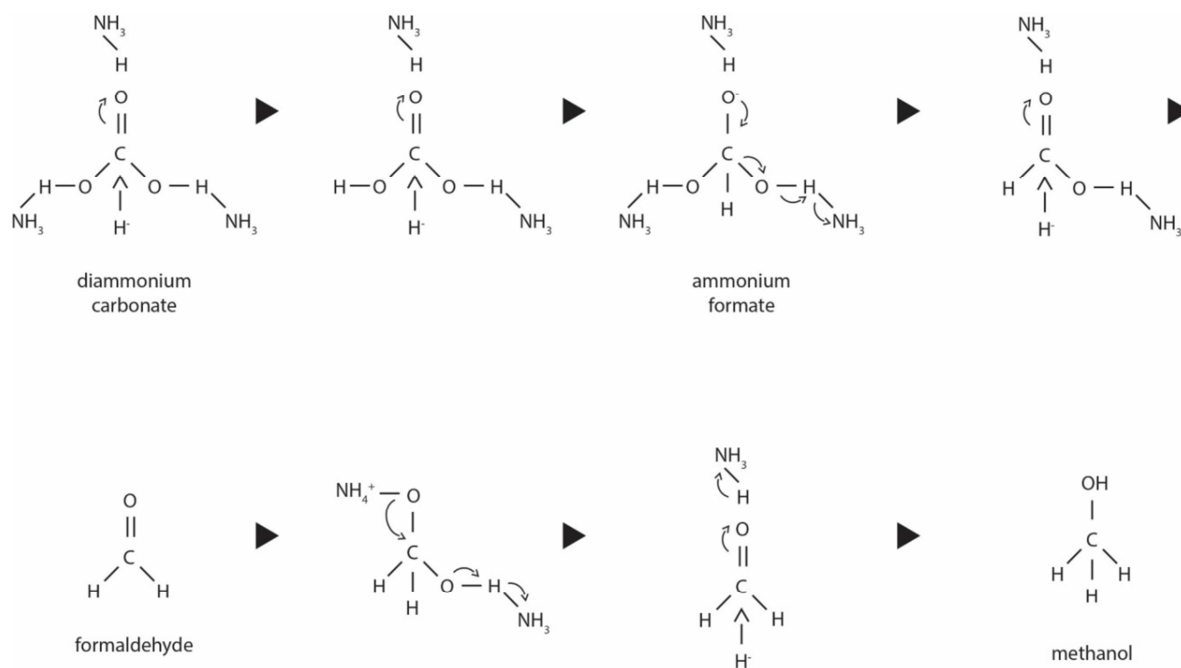


Figure 1. Possible mechanism for the sequestration of CO_2 and conversion to formic acid, formaldehyde and methanol in NaBH_4 in NH_4OH .

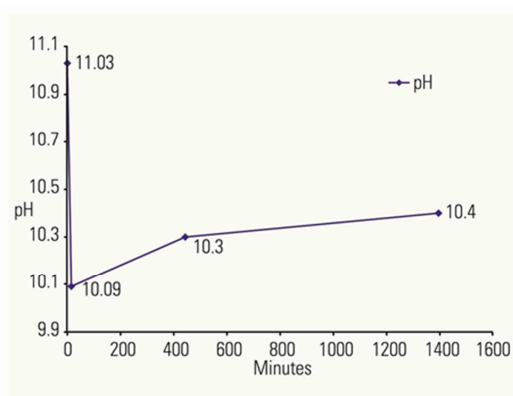


Figure 2. PH of the reaction of NaHCO_3 in $\text{NaBH}_4/\text{NH}_4\text{OH}$ solution versus time.

The pH of the reaction mixture dropped from 11.0 to 10.09 by the time a pH could be determined. The reaction mixture was monitored at various times and approached asymptotically to 11.03 over more than 20 hours. This reduction in pH could be explained by the consumption of H^- and the loss to the headspace of NH_4^+ to NH_3 (g). Because the reaction mixture is capped the pH can be maintained at a relatively high value, alkoxide can be maintained, and it eventually collapses to the carbonyl for both formic acid and formaldehyde. This allows collapse of the charge on one O

atom, making carbonyl, with the displacement of OH^- , when the pH is relatively high.

There is no free boric acid in the methylene chloride extract. B-H stretch is in the spectral range of an IR spectrum of 2900cm^{-1} to 2600cm^{-1} . There is no B-H stretch in the IR spectrum of the reaction extract in either of the $\text{NaHCO}_3/\text{NH}_4\text{OH}$ or sparged air/ NH_4OH reaction mixture extracts.

Boric acid has absorbance in the infra-red region at two sets of concomitant peaks. They are; (1) 1150cm^{-1} and 1410cm^{-1} and (2) 945cm^{-1} and 1150cm^{-1} . Although in the standard boric acid spectrum yields 1150cm^{-1} , close to the 1170cm^{-1} found in both reaction mixtures, there is no concomitant peaks for the 1150cm^{-1} , that is neither 945cm^{-1} nor 1410cm^{-1} . Therefore there is no free boric acid in the extracts of these reaction mixtures.

There is evidence for the presence of formic acid in each reaction mixture. With the sparged air/ NH_4OH , it is 2900cm^{-1} , and in the reaction mixture of the $\text{NaHCO}_3/\text{NH}_4\text{OH}$ reaction a peak at 2940cm^{-1} . Standard spectrum for formic acid has two peaks at 2913cm^{-1} and 2980cm^{-1} . Peaks at 680cm^{-1} and 1653cm^{-1} are found in standard spectrum for formaldehyde and in the IR spectrum of each reaction mixture there are two peaks, 640cm^{-1} and 1653cm^{-1} . The presence of these is a strong indication of the presence of formaldehyde in both reaction mixtures. The IR peak at 1170cm^{-1} is evidence that supports

the presence of methanol in the reaction mixture extracts. Acetone, added to extract as a standard, had peaks at 1210cm^{-1} and 1360cm^{-1} . Neither peak of the acetone interfered with the formaldehyde peak.

The solid crystals were identified after collection, washing with NH_4OH (1N) and drying at ambient temperature and pressure as ammonium pentaborate tetrahydrate. There is loss of a liquid at 104°C - 106°C . The liquid is presumed to be H_2O . Upon increasing the temperature beyond this point to 150°C there was no melting of the remaining white solid. Table 2 lists the melting points of several possible crystals. The loss of H_2O for ammonium pentaborate tetrahydrate is 110°C . Clearly small amounts of impurities in the isolated crystals could depress the loss of liquid point to what was observed. And impurities could widen the range of loss of liquid point as what is found for these isolated crystals.

The predicted yield of crystals for the $\text{NaHCO}_3/\text{NH}_4\text{OH}$ reaction mixture was 1099.5 mg from the solubility portion of Table 2, that is, $10.9\text{g}/100\text{mL}$. The soluble portion of this material is predicted to be 436 mg. Subtracting the soluble yield from the predicted yield for this reaction gives 635mg. We isolated 692mg of the crystals which is 4% higher than predicted, suggesting the borohydride is completely converted to ammonium pentaborate tetrahydrate. The 4% difference between predicted yield and found yield is well within the expected accuracy of the reaction and this experimental workup process.

4. Conclusion

Carbon dioxide from the air can be sequestered by sparging it through a solution of 1N NH_4OH . NaBH_4 is added to produce, over time, in a closed vessel, formic acid, formaldehyde, methanol and ammonium pentaborate tetrahydrate. Standard IR spectral absorbance comparisons to experimentally obtained IR spectral absorbance values demonstrate the identities of these valuable chemicals. The solid produced was identified, the white crystalline solid, as ammonium pentaborate tetrahydrate.

The ease of sequestration of CO_2 by sparging air into an NH_4OH aqueous solution and subsequent conversion to the valuable chemicals, noted above, by adding NaBH_4 to the mixture allows its consideration for a manufacturing process to relieve the burden of CO_2 accumulation in our atmosphere and oceans and could add fuel consumption assistance, to ease pressure on ethanol production and the US sustainable fuels necessities in the world.

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