Transactions of the Illinois Academy of Science
(1986), Volume 79, 1 and 2, pp. 67-70

HYDROGEN GENERATION AT ELEVATED TEMPERATURE WITH PRIMARY AND SECONDARY ALCOHOLS

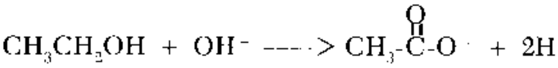
Robert C. Duty, Leo W. Halm and Paul J. Dambek
Chemistry Dept., Ill. State University
Normal, IL 61761

ABSTRACT

Hydrogen gas was liberated from protic solvents (alcohols) which contained α-hydrogens. Potassium hydroxide was the reactant required to produce hydrogen at temperatures of 200°C or higher. Alcohols studied in these reactions were ethyl, isopropyl, n-butyl and t-butyl alcohols. Temperatures varied from 150°C to 265°C.

INTRODUCTION

Several papers have appeared in the literature suggesting that hydrogen was generated from primary and secondary alcohols with alkali at elevated temperatures. Ross (1979) suggested that a hydride ion was responsible for the increase in solubilization of coal in pyridine when it was treated with sodium hydroxide in isopropyl alcohol as the solvent. Ouchi (1981) observed the same effect when he reported almost 100% solubilization in pyridine of young coals (C < 82 wt%) when they were reacted with alkali in ethyl alcohol. He attributed the increase in solubilization to hydrolysis accompanied by the formation of hydrogen from the ethyl alcohol.



$$CH_3CH_2OH\ +\ OH^-\ \text{----}>\ CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O^-\ +\ 2H$$

Ouchi also suggested methyl alcohol as a precursor to hydrogen in his Taiheiyo coal experiments which gave similar results to the ethanol reactions (1978). In all of Ouchi's experiments, he did not experimentally prove or measure the concentration of hydrogen. Consequently, in our experiments we have established unequivocally that hydrogen is produced from primary alcohols, and secondary alcohols, but not tertiary alcohols.

MATERIALS AND METHODS

The gas chromatographic column was a 2.5 cm (i.d.) × 2.9 m copper tube packed with molecular sieve, activated, Type 13X(40-60 mesh) absorbent (Panson, 1964). The column temperature was 100°C with a 60 ml/min flow rate of helium. Retention times were hydrogen, 1 min; oxygen 1.3 min; nitrogen 2 min and methane 3.2 min. The bomb used in these experiments was a Parr Bomb (Model No. 4714). The reactions were run with 1 g of potassium hydroxide and 30 ml of solvent. The solvent was purged with nitrogen prior to use, and the reaction vessel was purged with nitrogen before sealing the vessel.

The gas samples were collected directly from the Parr bomb after cooling. The samples were collected in rubber balloons, and the gas chromatographic gas syringe penetrated the balloon through a piece of scotch tape. Several samples could be taken from the balloon by this method.

The reaction times varied from 1 h to as long as 24 h. Pressure would rise rapidly (1 h to 250°) and the pressure for isopropyl alcohol was 1900 psi. It would rise slowly to reach its maximum pressure (2300 psi) when the reaction was stopped. No reactions were run to ascertain how high the pressure would reach. Other alcohols responded similarly to isopropyl alcohol. The results of these tests are given in Table I.

RESULTS AND DISCUSSION

In each case, hydrogen gas was generated for all solvents except t-butyl alcohol. However, below 200°C, the amount of hydrogen generated was negligible (less than 0.01 m moles). Small quantities of hydrogen also are generated after 1 h with ethyl and n-butyl alcohols where 0.166 and 0.306 m moles of hydrogen were produced, respectively. The t-butyl alcohol was the only alcohol which didn't produce hydrogen. This can be explained on the basis that it is a tertiary alcohol and does not possess an α-hydrogen which must be the precursor to the hydrogen radical. Isopropyl alcohol was not run at the 1 h reaction time.

Methane, albeit in small quantities, was formed in both isopropyl and ethyl alcohol, but not in n-butyl alcohol. This can be explained by the fact that the α-β carbon-carbon bond cleavage will produce a methyl radical with both isopropyl and ethyl alcohol, but with n-butyl alcohol an α-β bond cleavage would produce an ethyl radical. No evidence for ethane, however, was found in the gases produced from the n-butyl alcohol reaction. The α-β carbon-carbon bonds next to a heteroatom are more labile (Silverstein *et al.*, 1981), and results in the methane production.

Since hydrogen was generated with 1 g of potassium hydroxide, we reacted ethyl alcohol and n-butyl alcohol without the potassium hydroxide present. Both solvents, without the potassium hydroxide present, were reacted in the same manner as previously at a temperature of 250°C for 1 h. Hydrogen was present, but only in trace amounts (less than 0.01 m moles). Consequently, the alkali is undoubtedly responsible for the hydrogen gas generation in alcohol solvents as suggested by Ouchi *et al.*

We attempted to isolate the oxidized products from the reactions of ethyl and isopropyl alcohol which would be acetic acid and acetone, respectively. In each case the solvents (ethyl and isopropyl alcohol) were removed below 90°C by rotary evaporation. The distillate was analyzed by gas chromatography and indicated no peaks for acetone or acetic acid.

The distilland was dissolved in water and acidified with hydrochloric acid to neutralize any potassium acetate present. The acidified aqueous layer was extracted several times with diethyl ether in order to extract any acetone or acetic acid in the aqueous layer. A yellow color from the aqueous layer was extracted into the ether layer which was dried with anhydrous magnesium sulfate and rotary evaporated to dryness which left a yellow semisolid as residue. This yellow residue was run on the IR and NMR, and a carbonyl peak at 1720 cm^{-1} was observed for the ethanol residue and a carbonyl peak at 1660 cm^{-1} was observed for the isopropyl residue.

Both NMR spectra of the residues revealed unresolved multiplets in the aliphatic regions of the spectra. Consequently, since no trace of acetic acid or acetone were found, the oxidized products from ethyl and isopropyl alcohol must have formed condensed and/or polymeric compounds.

SUMMARY

Primary and secondary alcohols which contain α-hydrogens will liberate hydrogen in the presence of potassium hydroxide at temperatures between 200°C and 265°C, inclusively. Methane, in small quantities, was liberated with ethyl alcohol and isopropyl alcohol, but not n-butyl alcohol.

REFERENCES

Ouchi, K., Makabe, M. 1981. Effect of Pressure and Temperature on the Reaction of Coal with Alcohol-Alkali. *Fuel*, *60*, 327-29.

Ouchi, K., Fuse, S. and Makabe, M. 1978. Effect of the Species of Alklai on the Reaction of Alcohol-Alkali-Coal. *Fuel*, 57, 801-02.

Panson, A.G. and Adams, L.M. 1964. Complete Gas Chromatographic Analysis of Hydrogen in Fixed Gases and Hydrocarbons Using One Detector and Helium as Carrier Gas. *J. Gas Chromatog.*, *2*, 164-66.

Ross, D.S. and Blessing, J.E., 1977. Isopropyl Alcohol as a Coal Liquefaction Agent. *Am. Chem.Soc., Div. Fuel Chem.* 22 No. 2, 208-13.

Silverstein, R.M., Bassler, G.C. and Morrill, T.C., "Spectrophotometric Identification of Organic Compounds", 4th Edition, John Wiley & Sons, New York, N.Y., 1981 p. 14.

Table 1. Hydrogen Analysis*

Solvent	Temp.	Gases (m moles)**	Time of Reaction	Maximum Pressure (psi)
Ethyl Alcohol	240°	H_2(0.410) CH_4(0.017)	18 h	2,050
Ethyl Alcohol	200°	H_2(0.360) CH_4(0)	18 h	1,150
Ethyl Alcohol	150°	H_2(trace) CH_4(0)	18 h	200
Isopropyl Alcohol	250°	H_2(0.370) CH_4(0.171)	24 h	2,300
Isopropyl Alcohol	250°	H_2(0.282) CH_4(0.087) O_2(0)	18 h	1,550
Isopropyl Alcohol	200°	H_2(0.282) O_2(0.017) CH_4(0)	18 h	1,000
n-Butyl Alcohol	265°	H_2(0.306) CH_4(0)	1 h	1,860
Ethyl Alcohol	250°	H_2(0.166) CH_4(0)	1 h	2,025
t-Butyl Alcohol	250°	H_2(0) CH_4(0)	24 h	580

*reactions were run with 30 ml of solvent and 1 g KOH.

**reaction vessel was 52 ml in volume, and m moles were calculated from the volume precentages from the g.c. and the volume of gases in the Parr bomb (52 ml-30 ml).