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A Computational Study to Determine Thermodynamic Properties for Hydrogen Production from Sodium Borohydride Reaction †

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Abstract

Because of fossil fuel depletion and its inevitable hazard to the environment researchers have worked on alternative fuel sources like Hydrogen (H_2) which can be obtained via renewable energy sources like biomass, solar, geothermal, ocean, wind, hydropower, and nuclear. H_2 has many advantages. It has a high heating value compared to traditional fossil fuels. It can be synthesized from water or biomass without releasing any Greenhouse Gases (GHGs) Emission. Nowadays, the most popular hydrogen production methods are sodium borohydride ($NaBH_4$) hydrolysis, photocatalysis, and water electrolysis. Among them, the $NaBH_4$ hydrolysis reaction is preferred due to its advantages. It can be possible to reach high hydrogen generation rates under mild conditions with this reaction. In this work, thermodynamic analysis was carried out with Gauss software. At first, the products and reactants of the reaction were drawn. Then enthalpy and free energy information were taken for the reaction. Calculations were done via the Hartree-Fock Method for each molecule. Basis Set was selected as 6-31G(d). Reaction conditions were assumed as 298 K and 1 atm. As a result of the computations, the Enthalpy and Free Energy of the reaction were found as −58.0315 kcal/mol and −72.6141 kcal/mol respectively. This meant that this reaction was exothermic because of the negative sign of enthalpy. Besides that, the negative sign of Gibbs Energy was related to spontaneous reaction.

Keywords: $NaBH_4$ hydrolysis; thermodynamic analysis; H_2 production

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1. Introduction

Hydrogen is a fuel that has a low environmental impact. This means that after its burning, no CO_2 emissions occur. H_2 production can be achieved using several methods, such as water electrolysis, steam reforming, and coal gasification. Besides its production, transportation is another important research area for H_2. Its high flammability and low density cause difficulties in storing and transporting it over long distances. $NaBH_4$ is a chemical to be utilized in both the storage and production of hydrogen [1]. This reaction can be conducted in a non-catalytic or catalytic way at room temperature [2].

Thermodynamic modeling in a computational way of a given reaction enables observing the reaction system without making any experiments [3].

Quantum Chemical Methods can be applied to a process to define its thermodynamic properties. In this way, it is possible to determine the enthalpy and free energy of a given reaction. Gibbs Free Energy gives information about the probability of a reaction. Via GaussView Software, one can reach these values via non-empirical ways [4].

In this study, the aim was to determine the thermodynamic properties of the $NaBH_4$ hydrolysis reaction. The study was based on only computational studies.

2. Computational Method

Thermochemical values were computed in Gaussian software. First, every reactant and product was drawn. Regarding their calculation results, the Free Energy and Enthalpy of the reaction were determined. $NaBH_4$ hydrolysis reaction was as follows:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

3. Results of the Thermodynamic Study

For Gaussian calculations, firstly, molecules were drawn based on the reaction in GaussView. In Figure 1, images of each molecule with bond lengths in Å. Then calculations were done via the Hartree-Fock Method for each molecule. Basis Set was selected as 6-31G(d). Reaction conditions were assumed as 298 K and 1 atm. Gaussian Calculation Summary for each molecule was obtained as shown in Table 1. In this Table, ε_0, ε_{ZPE}, E_{tot}, H_{corr}, and G_{corr} mean the total electronic energy, zero-point energy of the molecule, total internal energy, correction to the enthalpy due to internal energy, and correction to the Gibbs free energy due to internal energy, respectively. The entropy and heat capacities of each molecule are presented in Table 1. Enthalpy of the reaction was calculated via Equation (1). It was computed by taking the difference between the heat of formation for products and reactants. The same way was applied to calculate the Gibbs Energy of the reaction by utilizing Equation (2). As a result of the computations, Enthalpy and Free Energy of the reaction were found as −58.0315 kcal/mol and −72.6141 kcal/mol, respectively. This meant that this reaction was exothermic because of the negative sign of enthalpy. The enthalpy value coincided with the literature [5]. Besides that, the negative sign of Gibbs Energy was related to a spontaneous reaction.

$$\Delta_r H^\circ\,(298K) = \Sigma\,\Delta_f H^\circ_{product}(298K) - \Sigma\Delta_f H^\circ_{reactant}(298K) = \Sigma\,(\varepsilon_0 + H_{corr})_{products} - \Sigma\,(\varepsilon_0 + H_{corr})_{reactants} \quad (2)$$

$$\Delta_r G^\circ\,(298K) = \Sigma\,\Delta_f G^\circ_{product}(298K) - \Sigma\,\Delta_f G^\circ_{reactant}(298K) = \Sigma\,(\varepsilon_0 + G_{corr})_{products} - \Sigma\,(\varepsilon_0 + G_{corr})_{reactants} \quad (3)$$

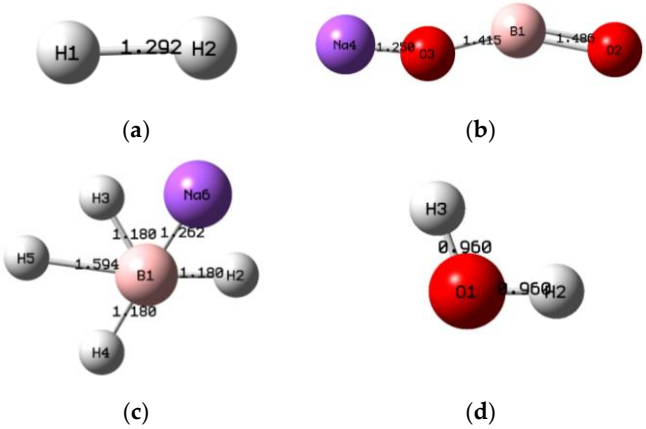

Figure 1. Related Molecules for $NaBH_4$ reaction (**a**) Hydrogen; (**b**) Sodium metaborate; (**c**) Sodium borohydride; (**d**) Water.

Table 1. Calculated thermochemistry values from Gaussian for sodium borohydride hydrolysis. All values are in Hartrees. (298 K, 1 atm).

	$NaBH_4$	H_2O	$NaBO_2$	H_2	Na	B	H	O
ε_0	−187.976351	−76.009862	−335.860216	−1.037482	−161.841435	−24.522037	−0.498233	−74.656604
ε_{ZPE}	0.050072	0.022129	0.009946	0.000000	0.000000	0.000000	0.000000	0.000000
E_{tot}	0.053187	0.024963	0.013374	0.002360	0.001416	0.001416	0.001416	0.001416
H_{corr}	0.054131	0.025907	0.014318	0.003305	0.002360	0.002360	0.002360	0.002360
G_{corr}	0.027274	0.004514	−0.015115	−0.012532	−0.015083	−0.014040	−0.010654	−0.013915
$\varepsilon_0 + \varepsilon_{ZPE}$	−187.926279	−75.987733	−335.850270	−1.037482	−161.841435	−24.522037	−0.498233	−74.656604
$\varepsilon_0 + E_{tot}$	−187.923163	−75.984899	−335.846842	−1.035121	−161.840019	−24.520621	−0.496817	−74.655188
$\varepsilon_0 + H_{corr}$	−187.922219	−75.983954	−335.845898	−1.034177	−161.839075	−24.519677	−0.495872	−74.654244
$\varepsilon_0 + G_{corr}$	−187.949077	−76.005348	−335.875331	−1.050014	−161.856518	−24.536078	−0.508887	−74.670519

The Gaussian software also gave the information about entropy and heat capacity values for each compound in the reaction. The values were presented in Table 2. The experimental data were found for Hydrogen as 53.14 J/gK for entropy and 10.16 J/gK for constant volume heat capacity in the literature [6]. So, the computational data nearly coincided with the experimental data.

Table 2. Entropy and heat capacity values for molecules in $NaBH_4$ hydrolysis.

Thermodynamic Property	Unit	Compound			
		$NaBH_4$	H_2O	$NaBO_2$	H_2
Entropy (S)	Cal/mol·K	56.526	45.027	61.947	33.331
Heat Capacity (C_v)		8.052	5.986	9.134	4.968

4. Conclusions

A computational thermodynamic study for $NaBH_4$ hydrolysis reaction was carried out. Thermodynamic analysis was carried out with Gauss software. Products and Reactants of the reaction were drawn. Then, the enthalpy and free energy information were taken for the reaction. Recently, computational studies have gained attention in chemistry. Especially, there is scarce information about thermodynamics studies for a given reaction via Gaussian software. So, this study can be accepted as novel. This approach can be applied to any reactions in the future because of the decrease in the number of chemicals and energy use in the research.

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Conflicts of Interest: The author declares no conflicts of interest.

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