Kinetics of Self-Hydrolysis of Concentrated Sodium Borohydride Solutions at High Temperatures

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1. Introduction

Hydrolysis of sodium borohydride ($NaBH_4$) solution over metal catalyst is accepted as a potential technology for delivering H_2 to portable fuel cells. However, unresolved issues such as minimizing the amount of water and the nature of hydration of metaborate by-products limit its hydrogen storage capacities. An alternative method, steam/water vapor hydrolysis, can enhance the hydrogen storage capacities without catalyst, if operating conditions can be optimized [1]. In this approach, solid $NaBH_4$ absorbs water and deliquesces, forming a highly concentrated viscous solution at near boiling point of water, followed by hydrogen evolution from the concentrated viscous solution. It is also well understood that self-hydrolysis occurs even at room temperature when $NaBH_4$ is mixed with water and the rate becomes significant at high temperatures. Self-hydrolysis must be arrested to increase the shelf-life of the solution.

The knowledge of the kinetics of self-hydrolysis of concentrated solutions at elevated temperature is thus crucial for: (1) developing steam/water vapor hydrolysis technology; and (2) handling and storage of $NaBH_4$solutions. Concentrated solutions have not been studied extensively so far and the reported studies, except two [2, 3], were for buffered dilute solutions of $NaBH_4$ (< 0.4 wt%) at low temperatures (< 25^0C). The present study reports the kinetics of self-hydrolysis of unbuffered, unstabilized concentrated $NaBH_4$ solutions (10-20 wt%) at high temperatures (25-80 ^{0}C) by a differential isothermal isoconversional method.

2. Theoretical

The $NaBH_4$ hydrolysis (self or catalytic) reaction occurs according to[4]:

$$NaBH_4 \text{ (aq or s)} + (2+x)\ H_2O(l) \longrightarrow NaBO_2.\ x\ H_2O \text{ (aq or s)} + \text{heat} \qquad (1)$$

Where, x is the excess hydration factor.

The mechanism of this process is highly complex and too complicated to be described by a kinetic model within the practical operating conditions [5]. The isoconversional method is often used to describe such kinetics, where, assuming a single step kinetic approximation, the rate expression is [6].

$$\frac{d\alpha}{dt} = k'_{ap}(T, C_0)\, f(\alpha) \qquad (2)$$

$k'_{ap}(T, C_0)$ is the apparent rate constant, which depends on temperature T and initial reactant concentration C_0, αis the extent of conversion and f(α) the conversion function representing the mechanism of the process.

The NaBH$_4$ hydrolysis process exhibits maximum rate at the beginning of the reaction, which decreases continuously with the extent of conversion. The most appropriate form of f(α)for such decelerating type process isthe ‘reaction order model’[7]:

$$f(\alpha) = (1 - \alpha)^m \quad (3)$$

Where, m is the reaction order.

Combining Eqs. (2)- (3), and considering the definition of extent of reaction α gives:

$$\frac{d\alpha}{dt} = k_{ap}(T)\, C_0^{m-1}\, (1 - \alpha)^m \quad (4)$$

Where,

$$k'_{ap}(T, C_0) = k_{ap}(T) * C_0^{\ m-1} \quad (5)$$

For a fixed conversion (α), Eq. (4) reduces to

$$\left(\frac{d\alpha}{dt}\right)_{\alpha} = k''_{ap}(T, \alpha)\, C_0^{m-1} \quad (6)$$

Where,

$$k''_{ap}(T, \alpha) = k_{ap}(T) * (1 - \alpha)^m \quad (7)$$

Equation (6), after a logarithmic transformation:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha} = \ln k''_{ap}(T, \alpha) + (m - 1) \ln C_0 \qquad (8)$$

For an isothermal process, the values of $\ln k''_{ap}(T, \alpha)$ and m are determined by Eq. (8) for each temperature andα, for different initial borohydride concentrations.

The temperature dependence of the rate constant k$_{ap}$(T) is then expressed by Arrhenius relationship:

$$k_{ap}(T) = A_{ap} \exp\left(\frac{-E_{ap}}{RT}\right) \quad (9)$$

The apparent activation parameters, i.e. apparent activation energy (E_{ap}) and pre-exponential factor (A_{ap}) are estimated by linear regression of $\ln k_{ap}(T)$ vs. 1/T data.

3. Results and discussion

3.1. Kinetic study

Effect of $NaBH_4$ conversion and temperature on reaction rate

The experimental kinetic data used werereported by Yu and Matthews [8], in which the evolution of metaborate formation and $NaBH_4$ consumption were generated *in-situ* by ^{11}B NMR technique for unbuffered, unstabilized 10, 15 and 20 wt% $NaBH_4$ solutions at 25, 60 and 80 ^{0}C. The estimated reaction rates from the experimental data for various $NaBH_4$ conversion, initial $NaBH_4$ concentration and temperature are given in Table 1. As evident, the reaction rate increases with both temperature and initial $NaBH_4$ concentration fora fixed $NaBH_4$ conversionand decreases with increase in $NaBH_4$ conversionfor a fixed temperature and initial $NaBH_4$ concentration. Table 1 is then exploited to determine the reaction order and apparent activation parameterswith respect to $NaBH_4$ conversion and temperature.

Table 1.Reaction rates for different $NaBH_4$ conversions at various temperatures and initial $NaBH_4$ concentrations.

$NaBH_4$ (wt %)	T(^{0}C)	Reaction rates (r, mol L^{-1} hr^{-1}) at various $NaBH_4$ conversions									
		5 %	10 %	15 %	20 %	25%	30 %	35 %	40 %	45%	50%
10	25	0.086	0.048	0.025	0.015						
15		0.136	0.080	0.037	0.027						
20		0.241	0.108	0.057	0.036						
10	60	0.637	0.559	0.485	0.415	0.345	0.273	0.210	0.158	0.110	0.100
15		0.740	0.654	0.569	0.483	0.398	0.317	0.242	0.181	0.144	0.130
20		0.897	0.797	0.697	0.598	0.499	0.402	0.310	0.227	0.160	0.143
10	80	2.209	2.089	1.970	1.848	1.723	1.597	1.468	1.340	1.201	1.062
15		2.384	2.241	2.130	1.981	1.862	1.720	1.687	1.470	1.352	1.232
20		2.698	2.555	2.410	2.264	2.115	1.964	1.810	1.653	1.493	1.326

Effect of $NaBH_4$ conversion and temperatureon reaction order

Fig. 1 shows the reaction order as estimated by linear regression of rate versus $NaBH_4$ concentration for various $NaBH_4$ conversions and. As seen, the reaction order remains constant at a given temperature irrespective of $NaBH_4$ conversion,while it decreases with increase in temperature irrespective of $NaBH_4$ conversion. The order decreases from first-to 0.25 with increase in temperature from 25 to 80 ^{0}C.The estimated rate constant, $k_{ap}(T)$ (not given),decreases with increase in $NaBH_4$ conversion at constant temperature and increases with temperature at constant $NaBH_4$ conversion.It is noteworthy that the variation of reaction order with temperature has been reported by Vyazovkin and Sbirrazzuolui [9] for complex epoxy-anhydride cure kinetics.

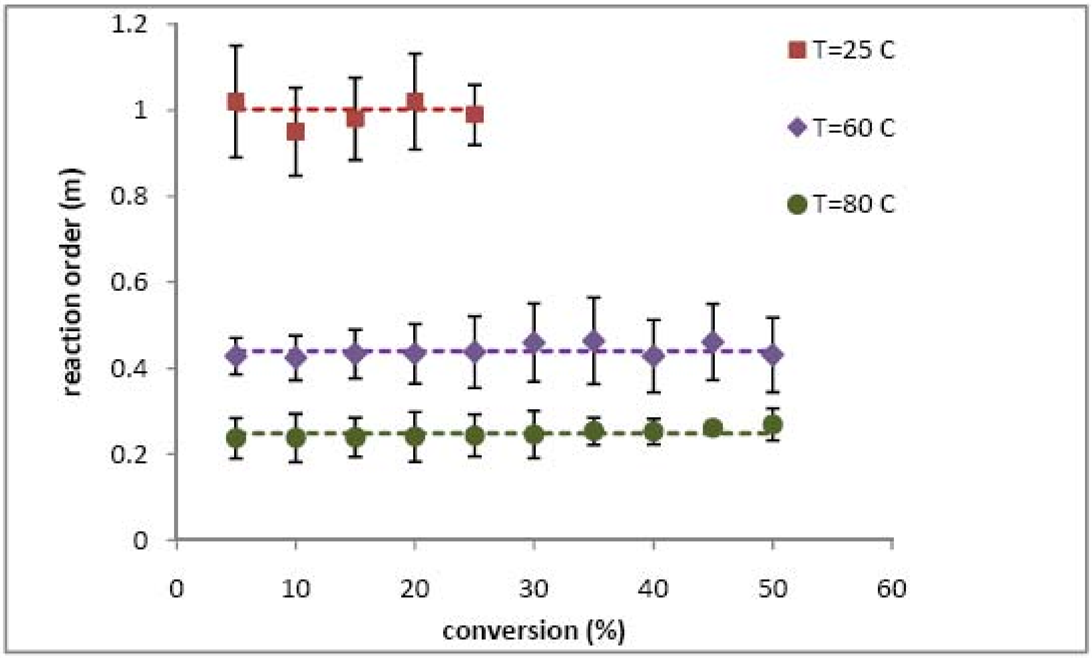

Figure 1. Effect of $NaBH_4$ conversion (%) on reaction order

It is well known that the solution viscosity increases during the course of hydrolysis reaction and this has been considered the reason for the observeddecrease in rate with reaction time or with $NaBH_4$ conversion[5].The effect of temperature on solution viscosity can be described in terms of Arrhenius-type relationships [10]:

$$\eta = \eta_0 \exp\left(\frac{E_{af}}{RT}\right) \qquad (10)$$

where$\eta$is the viscosity, η_0 the pre-exponential factor and E_{af} the activation energy of flow.This implies that increase in temperature decreases the solution viscosity. Viscosity is an indication of the solutionresistance to flow, and reduced flow resistance at high temperature enhancesthe interaction between reactant molecules. This in turnlessensthe relative contribution of the effect of the concentration on the reaction rate. The deviation from first-order kinetics at low temperatures to fractional-order kinetics at higher temperatures observed in the present study,is attributed to this difference in interaction between reactant molecules with respect to temperature due to change in solution viscosity.It is worthwhile noting that the earlier studies also reported first-order kinetics for self-hydrolysis of $NaBH_4$ for lower conversions and temperatures and for buffered solutions [11-15]

Effect of $NaBH_4$ conversion on activation energy

The classical kinetic theory defines reaction orders to beconstant with temperature.In the present case the observed difference in the reaction order with temperature (Fig. 1) suggests a $NaBH_4$conversion effect on the activation energy of the hydrolysis reaction (E_a), as given in Table 2. As seen, activation energy increases with $NaBH_4$ conversion/with formation of metaborate by-products.

It is well documented in literature that the formation of highly basic metaborate by-products in the course of the hydrolysis reaction results in highly viscous solutions. Investigation on the influence of soluble solids content on viscosity,by various researchers,showed that depending on the type of soluble solids content the activation energy of flow (E_{af}) might increase or decrease.The effects of soluble solid contents are described by the following expressions [10]:

$$\eta = \eta_1 C^{b_1} \qquad (11)$$

$$\eta = \eta_2 \exp(b_2 C) \qquad (12)$$

Where η_i and b_i are constants and C is the concentration. Hence one may assume that the activation energy of the flow increases with an increase in $NaBH_4$ conversion due to metaborate by-product formation, which in turn increases the activation energy of the hydrolysis reaction.

Table 2. Apparent activation energy determined for various $NaBH_4$ conversions

$NaBH_4$ Conversion (%)	${}^{a}E_{ap}$ (kJ mol^{-1})	R^2	Standard error	F	P-value
5	64. 43 ±14.5	0.9944	1.14	3914.89	0.025
10	71.03 ±11.5	0.9998	0.91	6721.39	0.038
15	82.50 ±13.5	0.9998	1.03	6725.19	0.008
20	89.62 ±12.5	0.9994	1.96	2152.88	0.013

[a]with ± 95% confidence interval

3.2. Modeling

The dependence of apparent activation energy (E_{ap}) on α(Table 2)is described by [16]:

$$E_{ap} = \varepsilon_0 + \varepsilon_1 \ln(1-\alpha) \qquad (13)$$

With ε_0 = 54.2 ± 1.7kJ mol^{-1} and ε_1= -114±12.2 kJ mol^{-1} (within a 95% confidence interval)

The change in apparent reaction order with temperature (Fig. 1) can be evaluated if the parameters of the kinetic compensation effect (KCE) are known [16]. The present study shows that $NaBH_4$ hydrolysis follows the following KCE relationship:

$$\ln A_{ap} = \alpha^* + \beta^* E_{ap} \text{ (14)}$$

With α^* =0.84 ±1.2 (mol $L^{-1})^{1-(m+n)}$ $hr^{-1}$and β^*= 0.36 ± 0.04kJ mol^{-1}(within a 95% confidence interval)

Combining Equations (4), (9), (13) and (14) results in:

$$\frac{d\alpha}{dt} = A_0 (1-\alpha)^{(m+n)} \text{ (15)}$$

Where:

$$n = \beta^* \varepsilon_1 - \frac{\varepsilon_1}{RT} \text{ (16)}$$

$$A_0 = \exp\left(\alpha^* + \beta^* \varepsilon_0 - \frac{\varepsilon_0}{RT}\right) C_0^{m+n-1} \text{ (17)}$$

Equation (15) shows that the overall process is apparently described with a reaction order n+m as illustrated in Fig 1.If the values of n are estimated from equation (16) and n+m from Fig 1, the values for m obtained are given in Table 3. As expected, m tends to a constant value, i.e. 0.22 ± 0.01.

Table 3.Values of n, n+m and m at different temperatures

$T(^0C)$	$n^{(1)}$ (Eq. 16)	$n+m^{(2)}$ (Fig. 1)	$m^{(3,*)}$
25	0.820	1.04	0.214
60	0.222	0.44	0.218
80	0.024	0.245	0.220

[1]dependent on temperature, [2]apparent reaction order
[3] independent on temperature, *m = 0.22± 0.01 (mean ± standard deviation)

4. Conclusions

The complex $NaBH_4$ self-hydrolysis process is analyzed by a differential isothermal isoconversional method, based on asingle-step kinetic approximation. The overall process is apparently described by a ‘reaction order’ model with temperature dependent reaction orderin a wide practical operating window (10-20 wt% $NaBH_4$ solution and 25-80 ^{0}C).

The apparent activation parameters, i.e. apparent activation energy and pre-exponential factor are conversion dependent and interrelated through the kinetic compensation effect, which explains the observed effect of the temperature on the reaction order.

The apparent activation parameters obtained provide some insight into the theoretical kinetic mechanism, which however remains a matter of heated debates.

5. References

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