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Bursting Dynamics in Molecular Hydrogen Generation *via* Sodium Borohydride Hydrolysis

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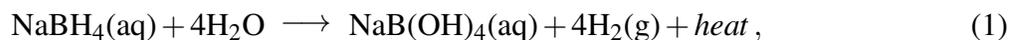
Abstract

The hydrolysis of borohydride salts is a promising process for the generation *in-situ* of pure molecular hydrogen that can be used as an alternative fuel. One of the obstacles toward its concrete application in the realm of green energy resides in nonlinear behaviours of H₂ delivery during the reaction development. In particular, we have recently shown that this system behaves like a chemical oscillator in a wide range of experimental conditions, exhibiting non-desirable fluctuations in the production of molecular hydrogen. Despite the potential of NaBH₄ hydrolysis in applicative terms, a deep understanding of the reaction mechanisms leading to these nonlinear dynamics is still left to a primary stage. Here we show how to control a typical bursting-like oscillatory scenario occurring in the gas development from NaBH₄ hydrolysis. Bursting transients are isolated and stabilized by using highly concentrated solutions of dihydrogen-phosphate/hydrogen-phosphate buffers with an initial pH value around 7. The length of the bursting transients critically depends upon the initial pH, the buffering strength and the working temperature. The stirring rate also influences this oscillatory dynamics. On the basis of the experimental evidence and NMR analysis of the reactive mixture, we hypothesise a possible kinetic scheme able to explain the onset of oscillatory instabilities.

Introduction

Transversal opinion is that we are at a critical point in terms of energy. On the one side many scientific evidence indicate that the exponential use of fossil resources increases CO₂ and other greenhouse gases in the atmosphere, thus provoking an increasing global warming and climate changes.¹ In parallel, there is a serious concern related to this massive exploitation of fossil fuels which, in turn, may be not available in the long period to satisfy the energy demand. Despite the urgent need for alternative and green solutions to this energetic issue, no unique resolved pathway has been proposed but, rather, a pool of partial solutions. Among these molecular hydrogen features one of the most concrete and promising. Molecular hydrogen can be easily converted into energy by using PEM fuel cells thanks to its oxidation with air, giving water as the main

28 by-product. Also, differently from other renewable sources of energy, molecular hydrogen can
29 be stocked and stored to be used when needed. Nevertheless a hydrogen-based energy economy
30 has not taken off due to important drawbacks. First, hydrogen has to be produced from other
31 substances and, typically, hydrogen generation is itself a source of greenhouse gases (consider
32 for instance steam-reforming processes). From the engineering viewpoint, H₂ storage is also a
33 challenging task, as it may involve pressurized containers with the gas extremely compressed or
34 liquefied, thus introducing safety problems. In this context, chemical compounds and, specifically,
35 boron-hydrides have met growing interest as a possible solution to the problem of hydrogen stor-
36 age.^{2,3} Among borohydride systems, sodium borohydride, NaBH₄, is viewed with interest because
37 of its considerable hydrogen gravimetric capacity, high stability in air, and low price. Hydrogen
38 generation *via* NaBH₄ follows two main routes: thermolysis and hydrolysis. The latter, globally
39 described by the reaction



40 is a spontaneous and exothermic reaction that works in mild conditions.⁴ This process yields
41 environmentally safe by-products (in particular borates that can be re-cycled) and features a con-
42 venient strategy for *in-situ* generation of highly pure hydrogen that can be used as a green fuel.⁵
43 Although reaction (1) appears to be an elementary process, it can present high kinetic complexity
44 and different practical problems, undesirable for potential applications. One is the low solubility of
45 NaBH₄ and of hydrated sodium metaborate (NaBO₂)⁶ which implies that a significant amount of
46 water is needed to conduct the reaction efficiently. A second issue is connected to the slow reaction
47 rate that calls for the use of proper catalysts to decrease the activation energy and accelerate the
48 hydrogen generation rate in controlled conditions. A further problem is represented by nonlinear
49 phenomena that can occur during the development of the reaction.^{7,8} Though never instigated in
50 depth, long-lasting periodic and more complicated oscillations have been shown in previous works
51 where NaBH₄ hydrolysis is performed in open conditions and in the presence of homogeneous

52 catalysts such as nickel complexes.^{9–11} Though many efforts have been devoted to enlighten the
 53 mechanism of the reaction,^{12–16} important kinetic details that can explain the onset of oscillatory
 54 behaviours are still scarcely understood.
 55 Recently we have systematically undertaken a kinetic study of NaBH₄ hydrolysis and shown that
 56 the non-catalysed hydrolysis can also exhibit oscillatory transients in the hydrogen generation.

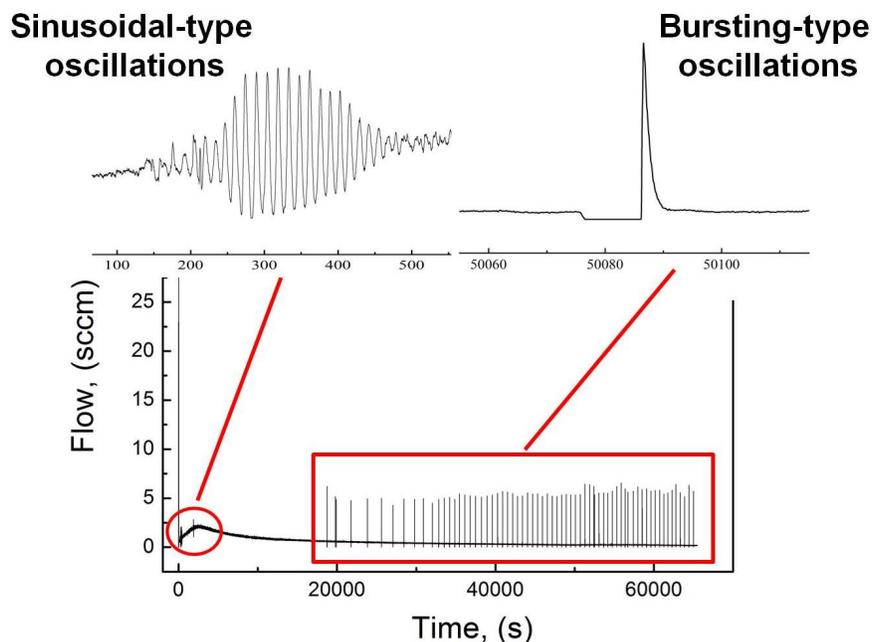


Figure 1: Example of gaseous H₂ out-flow in the non-catalysed NaBH₄ hydrolysis carried out with 1.5 g of NaBH₄ and 15 ml of distilled water (i.e. $c_{NaBH_4}=2.6$ M) at 30 °C. The dynamics can show two typical oscillatory scenarios: a sinusoidal-type transient and a bursting-type regime. Flow is given in standard cubic centimeters per minute (sccm).

57 Fig. 1 illustrates a time series of the gas delivered during NaBH₄ hydrolysis reaction, where
 58 two main oscillatory scenarios characterizing this system can be observed. One is a sinusoidal-
 59 type periodic transient that takes place at the very beginning of the process (after 150-200 s). This
 60 dynamics typically consists of around 10 oscillations with a characteristic period of 18 ± 2 s and
 61 an amplitude ranging between 0.5 and 2 sccm. The second scenario is a long-lasting bursting-type
 62 regime in which the oscillation pattern shows an initial decrease of the gas-flow, followed by a
 63 spike and, then, a relaxation phase. The amplitude of these oscillations is much larger than that ob-
 64 served in the sinusoidal-type scenario (it ranges between 5 and 20 sccm in the reaction conditions

65 considered).

66 In a previous study¹⁷ we focused on the sinusoidal-type transient. Thanks to a series of *ad-hoc*
67 experiments we gave evidence that this oscillatory behaviour is not the result of any instrumental
68 artifices or stochastic fluctuations but it rather features a deterministic phenomenon which can be
69 interpreted in the framework of nonlinear chemistry. We investigated the nature of these oscilla-
70 tions and we could disprove the possibility that flow oscillations were fueled by physical mecha-
71 nisms such as supersaturation that triggers gas oscillations in gas evolution oscillators (or bubble-
72 lator)^{18,19} or by a thermo-kinetic interplay. Also, we could infer that gas flow oscillations are most
73 probably driven by a chemical “oscillophor” in the reactive mixture.^{20,21}

74 While sinusoidal-type transients were controlled and characterized at a large extent, bursting-like
75 scenarios were found far less reproducible. In this work we isolate conditions for stabilizing and
76 controlling these oscillatory regimes. We deepen the role of the reactive mixture pH and the tem-
77 perature as critical parameters for the onset and the length of bursting regimes. Based on analytical
78 investigations, we finally propose a minimal mechanism which may explain the onset of oscillatory
79 instabilities in this system.

80 **Experimental**

81 Experiments were carried out in batch conditions in a 25 ml quartz (or plexiglass) cylindrical re-
82 actor (see a schematic of the setup in Fig. 1). We used different quantities of NaBH₄ (98% Sigma-
83 Aldrich, powder) in a fixed volume (15 ml) of fresh prepared NaH₂PO₄/Na₂HPO₄ pH buffers.
84 Buffer solutions were prepared by using 1.00 M solutions of NaH₂PO₄ and adding a proper vol-
85 ume of a 5.00 M NaOH solution to achieve the desired pH value. All reactants were commercial
86 grade and used without any further purification. Stock solutions of NaH₂PO₄ and NaOH were pre-
87 pared by weight before use. Deionized water from reverse osmosis (Elga, model Option 3), having
88 a resistivity higher than 1 MΩ, was used to prepare all solutions. NaBH₄ was kept under argon
89 atmosphere (specifically in a glove-box) in order to avoid the aging of the salt due to hydration.

90 NaBH₄ fine powder was loaded into the reactor under argon atmosphere and the buffer solution
91 was successively injected with a syringe from a valve placed at the top of the reactor. The reactive
92 mixture was thermostated in a water bath. Typical experiments were performed at 30 ±1 °C. How-
93 ever various working temperatures have been considered and different stirring rates were applied
94 to the solution *via* a programmable magnetic stirrer. The gas developed by NaBH₄ hydrolysis was
95 piped through a Teflon tube into a flow-meter (Bronkhorst F-101, 0.1 %FS accuracy) interfaced
96 with a personal computer that allows to follow the flow dynamics. We also monitored the solution
97 and the bath temperature by means of two thermocouples. The dynamical profiles of the solution
98 and the bath temperature were collected by means of an acquisition card (National Instruments)
99 interfaced with a second PC.

¹¹B NMR analyses were performed by using a quartz tube to avoid possible interferences of glass-

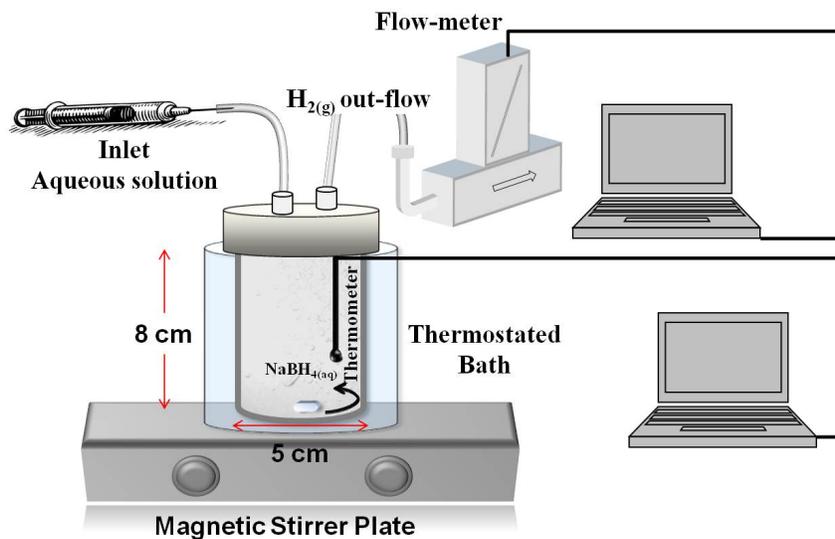


Figure 2: Sketch of the experimental setup.

100

101 made tubes in the detection of boron-based species. The solution for NMR analysis was prepared
102 by using 3 ml of water (90 wt% H₂O and 1 wt% D₂O) and 0.5 g of NaBH₄. The percent of
103 deuterated water should be limited since it enhances and modify the hydrolysis kinetics. Water
104 was poured into the quartz NMR-tube immediately before the analysis start. Gas evolution does
105 not affect significantly the quality of the spectrum.

106 **Experimental results**

107 **Influence of the pH**

108 NaBH₄ hydrolysis and the related production of gaseous molecular hydrogen are strictly sensitive
109 to the solution pH. To be more precise, the process is favoured in acidic conditions and inhibited
110 in a highly alkaline environment (pH > 10.5). In the absence of any buffering, as the reaction is
111 initiated, the pH of the system increases from a weakly acidic range to the interval 9.00–10.5, where
112 the pH variation is much slower. The dependence of H₂ generation on the pH in borohydrides
113 hydrolysis is embedded in the classical kinetic scheme used to describe the reaction:^{12–14}



114 where H₃BO₃ progressively converts into sodium metaborate and tetrahydroborate while pH in-
115 creases. It can be observed that H⁺ fuels the conversion of NaBH₄ into molecular hydrogen.
116 Intuitively the pH of the reactive mixture and its change in time also play a role in the oscillatory
117 instabilities. In our previous investigations we already tried to understand how the solution pH
118 impacts the onset of the oscillations and whether buffering the solution pH can stabilize oscillatory
119 transients. To this aim, we followed the dynamics of the reaction performed in alkaline buffers
120 (pH range [9.70, 11.50]) by using carbonate-bicarbonate pH buffers. MgCO₃ is in fact present
121 as an anti-caking agent in the NaBH₄ powder at hands (0.4 - 0.8 %) and could act as a buffer in
122 the reaction mixture. As expected, no oscillations were found by using buffer solutions with a pH
123 > 10.50. However we could not find any characteristic oscillatory behaviour even by buffering the
124 system below pH = 10.00, where regular oscillations were supposed to develop.

125 In this work we deepen the effect of pH as a critical parameter and stabilizing agent for oscillations

126 by using a different buffer, namely the $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ system. This pH buffer allows us to
127 work with more acidic initial pH values, typically in the range [5.00-8.00) (the pK_a of H_2PO_4^-
128 is around 7.2). Furthermore, as compared to our previous exploration, we use more concentrated
129 buffer solutions (~ 1 M) to increase the pH buffering strength of the reactive solution. The solu-
130 bility of NaBH_4 is not significantly affected by this fact.

131 In Fig. 3.a we resume the typical dynamics obtained when the reaction is performed with 1.5 g of
132 NaBH_4 and 15 ml of 1 M $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer solution (i.e. $c_{\text{NaBH}_4}=2.6$ M) at 30 °C and
133 under 1000 rpm stirring. The introduction of the buffer critically affects the process evolution. In
134 particular it triggers the onset of gas oscillations, which start immediately upon injection of the
135 buffer solution. In these conditions bursting-type regimes can be isolated with a high reproducibil-
136 ity. The initial pH of the buffer solution can change the characteristics of the oscillatory pattern and
137 the dynamics. Though the time series is strongly non-stationary (oscillations rely on a decreasing
138 baseline) due to reactant consumption, we can clearly observe that the length of the bursting tran-
139 sient increases by increasing the initial pH in the range [5.00, 7.00] and becomes maximal around
140 $\text{pH}=7$. This trend, quantitatively analysed in Fig. 3.b, can be ascribed to the maximal buffering
141 strength of the solution close to the pK_a of H_2PO_4^- . The system is, in fact, kept in quasi-stationary
142 weakly alkaline conditions in which oscillations appear favoured for a longer period. Beyond this
143 pH value, we obtained mainly erratic and scarcely reproducible evolutions of the gas. Finally, note
144 that this buffering of the reactive mixture suppresses sinusoidal-type oscillations.

145 The effective importance of the pH buffering strength in terms of stabilization of the oscillatory
146 regime was also confirmed by comparing experiments carried out with a decreasing concentration
147 the buffer solution. We observed that less concentrated buffers induce shorter oscillatory transients
148 characterized by a smaller amplitude and, in the limit case of pure water (in other words, with a
149 solution with a null buffering strength), the occurrence of these bursting regimes is statistically
150 irrelevant.

151 **Influence of the stirring**

152 A further experimental factor that can affect the oscillatory gas out-flow dynamics when the re-
153 action is carried out with $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffers is the stirring rate of the reactive mixture.

154 Similarly to the initial pH, this parameter influences both the length and the oscillation frequency
155 of the bursting transient. In Fig. 4.a we compare the reaction dynamics for increasing values of
156 the stirring rate. Experiments were performed at 30 °C with 1.5 g of NaBH_4 and 15 ml of a buffer
157 solution 1 M of NaH_2PO_4 (i.e. $c_{\text{NaBH}_4}=2.6$ M, initial pH = 7.00). An increase of the oscillatory
158 transient length (see Fig. 4.b) is observed while augmenting the stirring rate.

159 Indeed, the dependence of the dynamics upon the stirring rate should not be confused with the
160 critical effect that stirring exerts in gas evolution oscillators (bubblelators).^{18,19} In bubblelators an
161 improper stirring, either too fast or too slow, kills the onset and the persistence of the oscillatory
162 development of bubbles. As we did in our previous investigation,¹⁷ we checked this fact by also
163 following the system dynamics when a glass powder is introduced in the reactive mixture. In a real
164 bubblelator the presence of such heterogeneities creates nucleation points, thus avoiding the possi-
165 bility for gas supersaturation in the solution which is at the basis of the oscillatory mechanism. In
166 our system we could not reveal any difference between these dynamics with those characterizing
167 the glass-powder-free system. In the context of NaBH_4 hydrolysis, stirring has no critical effect on
168 the onset of the oscillatory instability but it rather promotes and homogenize the gas delivery from
169 the reactive mixture.

170 **Influence of the NaBH_4 initial concentration**

171 A typical feature of chemical oscillators is the dependence upon the concentration of the initial re-
172 actants. In batch chemical oscillators, the main reactant concentration acts as a *pseudo-parameter*
173 able to control the properties of chemical oscillations during the reaction development, even af-
174 fecting the possibility for the oscillatory instability to occur.²²⁻²⁶ In the system under analysis, we
175 explored the influence of the initial reactants by changing systematically the amount of NaBH_4 in
176 a fixed volume (15 ml) of 1 M $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer solutions. Experiments were performed

177 at 30 °C, with a stirring rate equal to 1000 rpm and initial pH = 6.00. The flow dynamics presents a
178 clear sensitivity to the initial concentration of NaBH₄. We also observe that oscillation frequency
179 decreases when lowering NaBH₄ initial concentration and, as expected, the bursting oscillations
180 persist longer while increasing NaBH₄. This feature is shown in Fig. 5.a where we report the tem-
181 poral evolution of the gas out-flow for different concentrations, c_{NaBH_4} , of the NaBH₄ solutions
182 and the related characterization is illustrated in Fig. 5.b. No oscillations can be found below the
183 critical threshold $c_{NaBH_4} < 0.9$ M.

184 **Influence of the bath temperature**

185 The temperature at which the reaction is carried out also plays a crucial role in the onset of the
186 oscillatory instability. In Fig. 6 we show the H₂ out-flow dynamics obtained from experiments
187 performed at different temperature with 1.5 g of NaBH₄ and 15 ml of a buffer solution 1 M of
188 NaH₂PO₄ (i.e. $c_{NaBH_4}=2.6$ M, initial pH=6.00 and a stirring rate equal to 1000 rpm). Bursting
189 dynamics occur when the temperature is larger than 30 °C ±0.5, while erratic behaviours can be
190 found if the working temperature is below this threshold. As the working temperature is led beyond
191 30 °C, the flow baseline is shifted to higher values, and the oscillation frequency and amplitude
192 also increase. By contrast the length of the transient shrinks, indicating that the amount of gas
193 delivered in this initial reaction phase tends to be conserved.

194 A further indirect evidence of the thermal influence on the system dynamics has been also pointed
195 out by changing the material of the reactor. In check experiments, we compared the typical dy-
196 namics resulting from NaBH₄ hydrolysis conducted in analogous conditions but in a reactor made
197 of quartz and in another one made of plexiglass. The oscillatory transient was found to be shorter
198 for the experiments in the quartz reactor, as it is able to dissipate faster the heat developed during
199 the exothermic hydrolysis process.

A possible mechanism for oscillations

Permissible species

In the light of the experimental evidence found in this and previous studies,¹⁷ gas out-flow oscillations in NaBH₄ hydrolysis appear coupled to an 'oscillating chemical core' in the homogeneous phase of the reactive mixture. If we stick to the reaction scheme (2–4), the set of species that can be involved in such a nonlinear mechanism in NaBH₄ hydrolysis is restricted to (i) the initial reactants, NaBH₄ and water (protons and hydroxides), (ii) the reaction products, metaborates and H₂, and (iii) the intermediates BH₃ and BH₅. In batch chemical oscillators the initial reactants and the ultimate products can follow step-wise concentration evolutions over a decreasing or an increasing monotonic trend, respectively. Indeed, initial reactants represent the engine of the oscillatory mechanism while only reaction intermediates can take effectively part to the oscillatory mechanism. The smooth and monotonous pH variation in the course of the reaction excludes that H⁺ or OH⁻ are involved in the oscillatory dynamics. BH₅ is a fast transient species and only BH₃ features a reliable oscillatory chemical variable.

However an oscillatory instability implies the presence of, at least, two oscillatory intermediates. Recent ¹¹B NMR inspections on the NaBH₄ hydrolysis mixture have shown that the species BH₃OH⁻ also forms during the hydrolysis reaction. In this study we have confirmed this result and in Fig. 7 we report the proton coupled ¹¹B NMR spectrum. The main signals, the singlet at 1.6 ppm and the quintet at -42.1 ppm, correspond to NaB(OH)₄ and BH₄⁻, respectively. Perusal of Fig. 7 at -13.5 ppm allows us to appreciate a small quartet over the noisy base line of the spectrum. This signal is related to the species BH₃OH⁻, while no other hydroxyborate can be detected. BH₃OH⁻ can feature a second candidate as an oscillating intermediate species.

Implemented kinetic scheme

According to the general theory on chemical oscillations,^{22,27,28} in order to meet conditions for oscillations in homogeneous phase, one nonlinear step such as an autocatalysis or an isomorphic

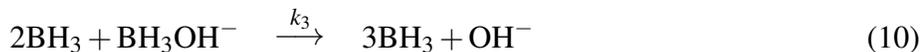
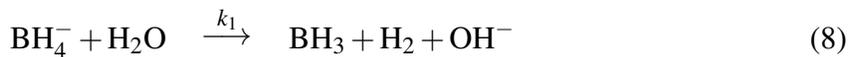
225 process must be at play. However kinetic model (2–4) consists of a set of pseudo-first order ele-
 226 mentary steps that cannot explain the emergence of oscillatory instabilities. Following the kinetic
 227 scheme proposed by Lefever et al.²⁹ to interpret and decompose a third-molecular step, we hy-
 228 pothesise a possible cubic autocatalysis in NaBH₄ hydrolysis by coupling the equilibrium between
 229 BH₃ and B₂H₆ with an isotopic exchange mechanism between the latter and BH₃OH⁻:



230 Assuming that step (5) develops with a significantly different temporal scale as compared to step
 231 (6) and is quickly reaching a stationary state, we can apply the standard adiabatic approximation,²⁹
 232 $d[\text{B}_2\text{H}_6]/dt = 0$, and re-write the global step as



233 On the basis of these considerations, we propose here an implementation of kinetic model (2–4)
 234 by introducing the globally auto-catalytic step (7):



235 where P represents the final product (namely boric acid or sodium metaborate or tetrahydrob-
 236 orate depending on the pH. This does not affect the system dynamics). Here BH₄⁻ maintains the

237 system in far-from-equilibrium conditions and, assuming a stationary description of the oscillatory
 238 regime (i.e. with the reactant slowly depleted), its concentration can be assumed as a constant.
 239 In the same way, $[\text{OH}^-]$ is taken as a constant, since the experiments suggest that oscillatory dy-
 240 namics occur in an optimal, slightly alkaline pH range. The steps describing the formation and
 241 the consumption of the fast chemical variable BH_5 have been included in reaction (8). The set of
 242 kinetic equations corresponding to the new kinetic mechanism now reads

$$\frac{d[\text{BH}_3]}{dt} = k_1[\text{BH}_4^-] - (k_2 + k_4)[\text{BH}_3] \quad (12)$$

$$+ k_3[\text{BH}_3]^2[\text{BH}_3(\text{OH})^-]$$

$$\frac{d[\text{BH}_3(\text{OH})^-]}{dt} = k_2[\text{BH}_3] - k_3[\text{BH}_3]^2[\text{BH}_3(\text{OH})^-] \quad (13)$$

$$\frac{d[\text{H}_2]}{dt} = k_1[\text{BH}_4^-] + 3k_4[\text{BH}_3] \quad (14)$$

243 Kinetic equation (14), describing H_2 production, is decoupled to the first two functions and, thus,
 244 the system dynamics can be reduced to equation set (12–13). Within this description, when the
 245 condition for the Hopf instability,

$$[\text{OH}]_c^- > (k_1^2 k_3 [\text{BH}_4^-]^2 + k_4^3) / (k_2 k_4^2), \quad (15)$$

246 is satisfied,^{22,29} chemical variables $[\text{BH}_3]$ and $[\text{BH}_3\text{OH}^-]$ can oscillate. The sub-system (12–13)
 247 acts as a minimal oscillophor which provides the driving force for hydrogen flow oscillations and
 248 represents here a general proof of concept that sodium borohydride hydrolysis can undergo an
 249 oscillatory instability. At this stage the model cannot be asked for a quantitative agreement with
 250 the experimental observable which is the out-flow of gaseous H_2 . Indeed, the kinetic constants
 251 are unknown and the kinetics ruling the gas delivery from the solution may be a complicated
 252 function of both the stirring rate and the temperature. In this sense a direct comparison between
 253 experimental dynamics and simulations of eqs. (12–13) can be misleading and is not included

254 in this paper. Nevertheless this kinetic scheme represents a solid basis able to explain important
255 features of the system observed in the experiments. It can predict for instance a lower pH threshold
256 for the emergence of an oscillatory behaviour while an upper pH threshold is *vice versa* dictated by
257 the fact that the reaction becomes inhibited when the pH approaches 10.5. In the weakly alkaline
258 pH regime the oscillatory species BH_3OH^- can form and a minimal amount of this intermediate
259 appears crucial to initiate oscillations. Also, from the analysis of kinetic equations (12–13) one can
260 expect²² that the oscillation frequency augments with the initial concentration of the main reactant
261 and this feature favourably compares with what observed in the experiments.

262 **Concluding discussion**

263 The NaBH_4 hydrolysis is a promising process for the *portable* generation of a green and alter-
264 native fuel, molecular hydrogen. To open such a perspective, a robust control of the kinetics of
265 gas formation is needed. In this and in a previous paper¹⁷ we have shown that this reaction may
266 presents deterministic nonlinear behaviours in a wide range of experimental conditions and two
267 typical oscillatory scenarios in the delivery of gaseous molecular hydrogen have been identified.
268 Despite the impact that such oscillatory dynamics may present in applicative terms, a complete
269 kinetic picture to explain these phenomena is still missing. Here we have focused on bursting-type
270 dynamics which were previously found difficult to be isolated. We have stabilized in a repro-
271 ducible way the conditions for this oscillatory instability by performing experiments with highly
272 concentrated $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ pH buffers which allowed us to increase the buffering strength.
273 Bursting oscillatory transients were critically sensitive upon the initial pH, the buffering strength
274 and the working temperature. In particular vigorous and high frequency oscillations appear and
275 damp down quite fast in weakly acidic conditions. Conversely, bursting transients are stabilized
276 (transient oscillations persist longer) within a slightly alkaline pH range around 7.2, where the
277 buffering strength is maximal and the reaction maintains quasi-stationary conditions for a longer
278 period. The system undergoes bursting-type oscillations beyond the threshold temperature 30 °C

279 ± 0.5 and long-lasting oscillations are also favoured by high stirring rates.
280 Based on the experimental dependences and ^{11}B NMR analytical investigations of the reactive
281 mixture, we have proposed a possible kinetic scheme consistent with the mechanism given in the
282 literature for this reaction. Specifically, we have implemented an autocatalytic step involving in-
283 termediates BH_3 and BH_3OH^- , which may explain the onset of oscillations. The resulting kinetic
284 scheme, isomorphic with another prototypical model for oscillations, the Brusselator,²⁹ captures
285 the need for slightly alkaline conditions, in which the critical intermediate BH_3OH^- forms. Our
286 model also substantiate the importance of the buffering strength to maintain optimal chemical con-
287 ditions for the oscillatory instability and to avoid a fast evolution towards too basic pH values
288 where the reaction is inhibited. The increase of the oscillation frequency as a function of the ini-
289 tial reactant concentration characterizing this model also compares favourably with experiments.
290 Within our description, H_2 does not play any active role in the oscillating mechanism but is cou-
291 pled and driven by the chemical *oscillophor* in the reactive solution. Further studies to support this
292 implemented model are in progress *via* a systematic characterization of the essential kinetic steps,
293 with a particular focus on the autocatalytic one. To this end other convenient precursors of the
294 intermediates of interest BH_3OH^- , such as NH_3BH_3 , are under consideration. Finally, this study
295 also features an important contribution in the context of nonlinear chemistry as NaBH_4 hydroly-
296 sis represents an original chemical oscillator that challenges us with a completely new chemistry
297 (based on boron compounds) with respect to known oscillators.

298 **Acknowledgement**

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302 IV Capitale Umano, Obiettivo Operativo 1.3 Linea di Attività 1.3.1 del P.O.R. Sardegna F.S.E.
303 2007/2013 - Progetti in forma associata e/o partenariale C.U.P. E85E12000060009”.

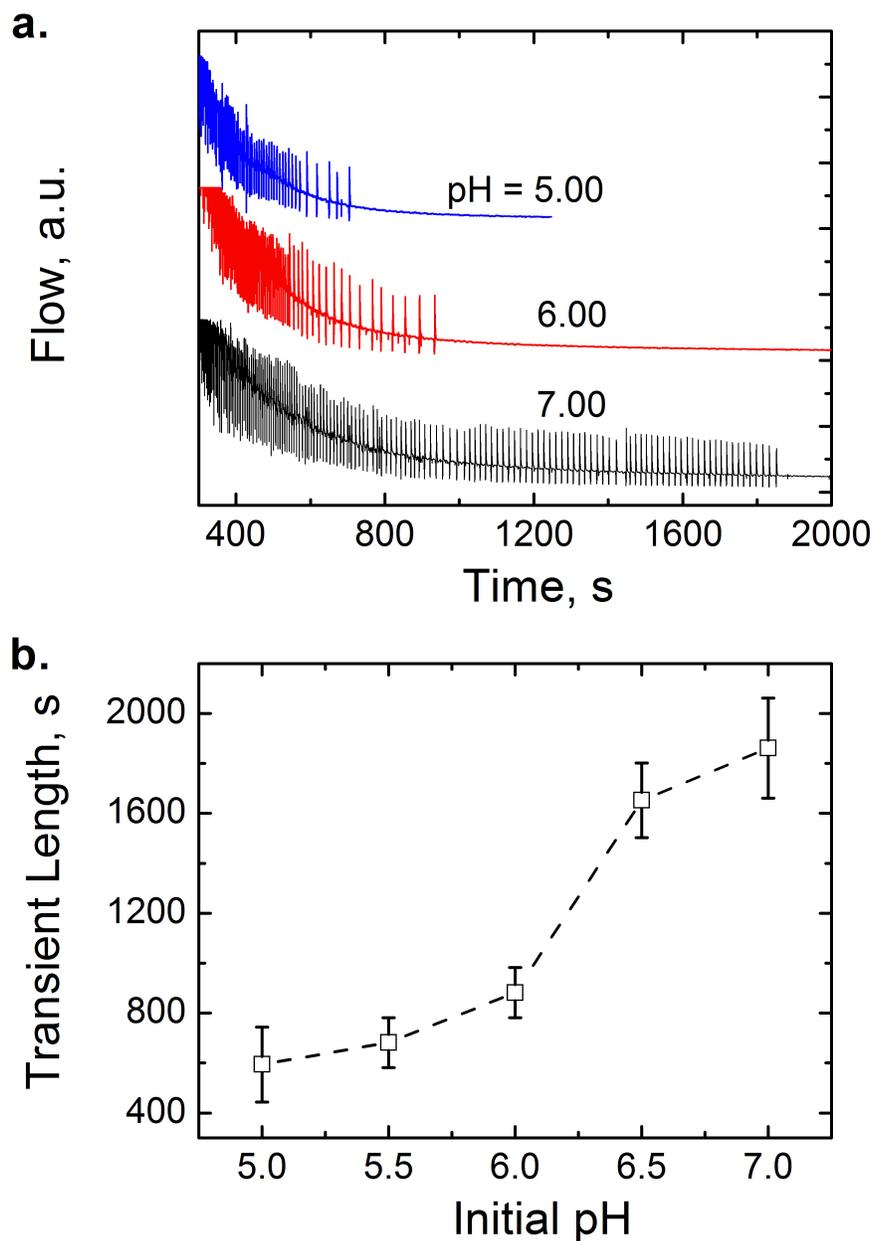


Figure 3: Dependence of H_2 flow dynamics upon the initial pH of $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer. Experiments were performed at $30\text{ }^\circ\text{C}$ with 1 M buffer solutions of NaH_2PO_4 and 2.6 M of NaBH_4 . The stirring rate is 1000 rpm. The initial pH of the solution was varied in the interval [5.00, 7.00] and the resulting dynamics are compared over an arbitrary flow scale in panel (a). Typical excursions of the bursts range in [5-20] scfm. Panel (b) shows a characterization of the oscillatory transient length as a function of the buffer pH. Each point is an average value of 3 experiments.

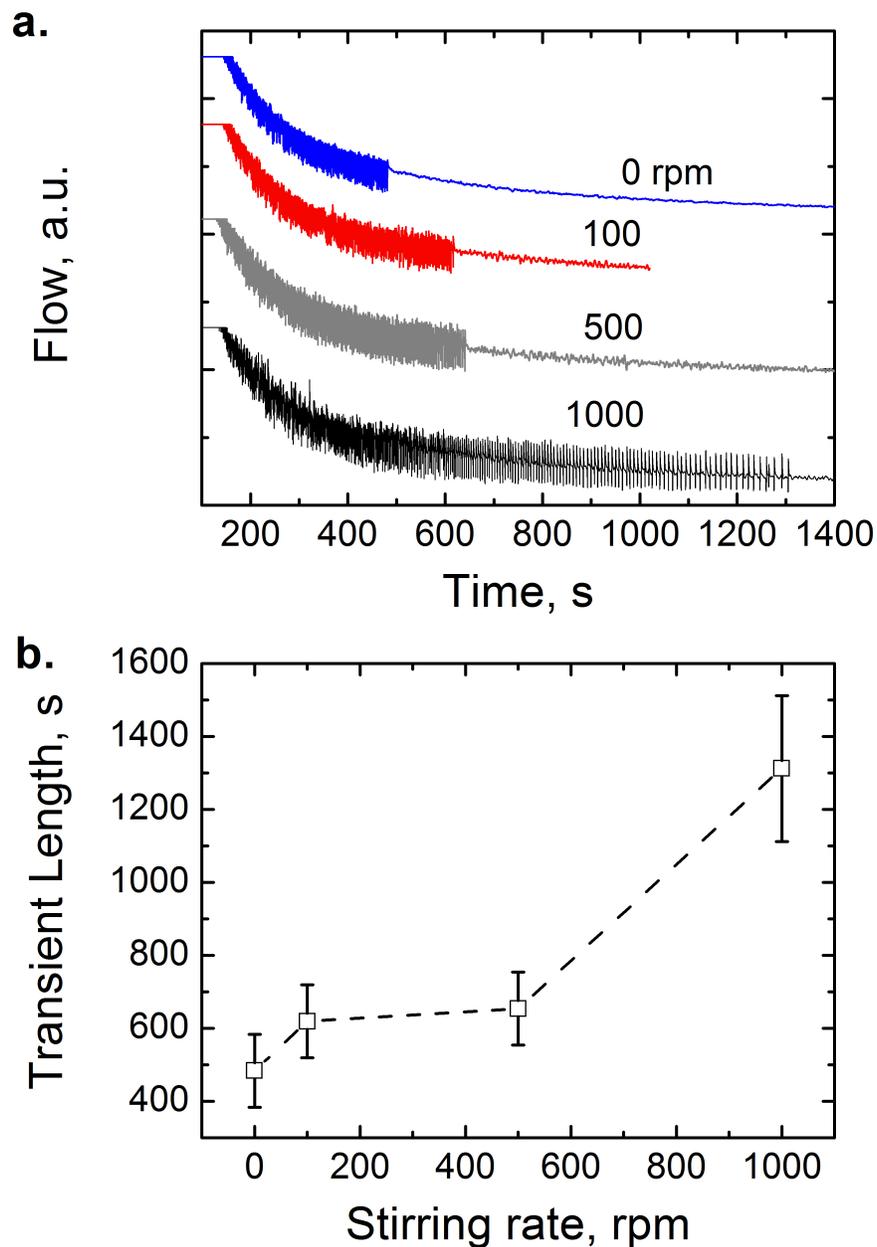


Figure 4: Dependence of H_2 flow dynamics on the stirring rate. Experiments were performed at 30°C with buffer solutions in concentration 1 M of NaH_2PO_4 and 2.6 M of NaBH_4 , $\text{pH} = 7.00$. The stirring rate was varied between 0 and 1000 rpm and the resulting dynamics are compared over an arbitrary flow scale in panel (a). Panel (b) shows a characterization of the oscillatory transient length as a function of the stirring rate. Each point is an average value of 3 experiments.

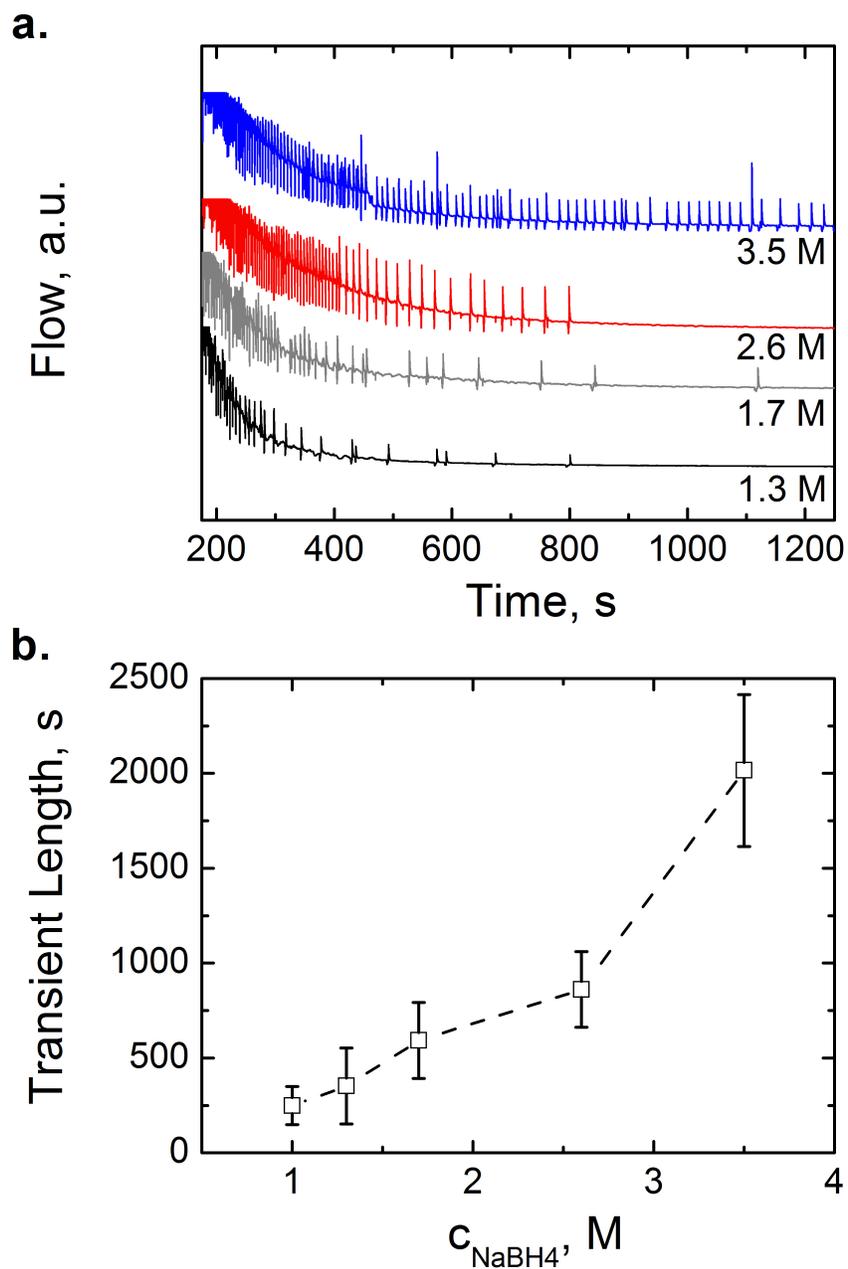


Figure 5: Dependence of H_2 flow dynamics upon the initial concentration of NaBH_4 . Experiments were performed at $30\text{ }^\circ\text{C}$ with buffer solutions 1 M of NaH_2PO_4 and 1.3 M , 1.7 M , 2.6 M and 3.5 M of NaBH_4 . The stirring rate was 1000 rpm and the initial $\text{pH}=6.00$. The resulting dynamics are compared over an arbitrary flow scale in panel (a) and the related transient lengths are characterized in panel (b). Each point in (b) is an average value of 3 experiments.

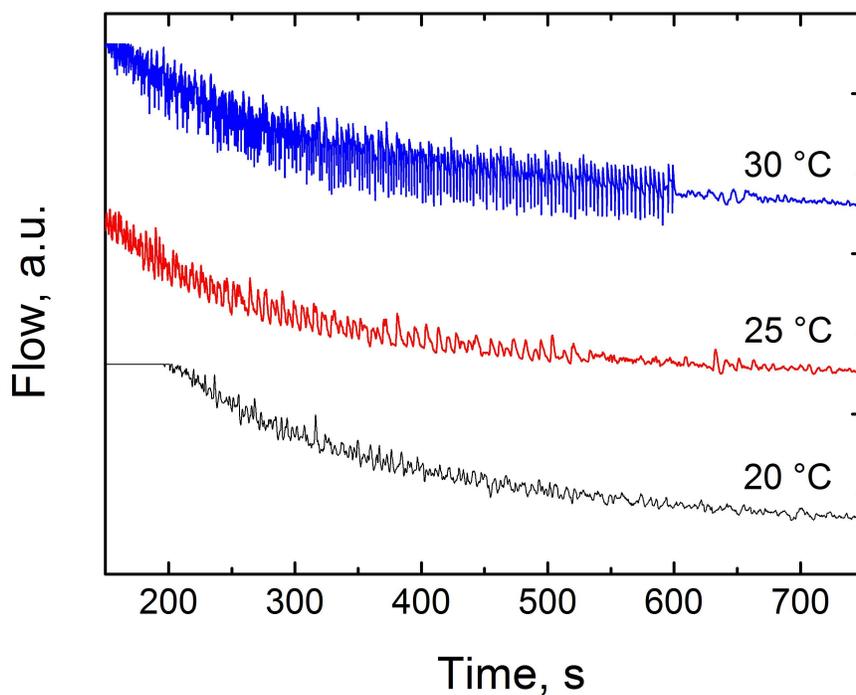


Figure 6: Dependence of H₂ flow dynamics upon the working temperature. Experiments were performed with 1.5 g of NaBH₄ and 15 ml of buffer solution 1 M of NaH₂PO₄ (i.e. $c_{NaBH_4}=2.6$ M, pH=6.00 and the stirring rate was 1000 rpm). Bursting-type oscillatory transients appear in a reproducible way beyond 30 ± 0.5 °C.

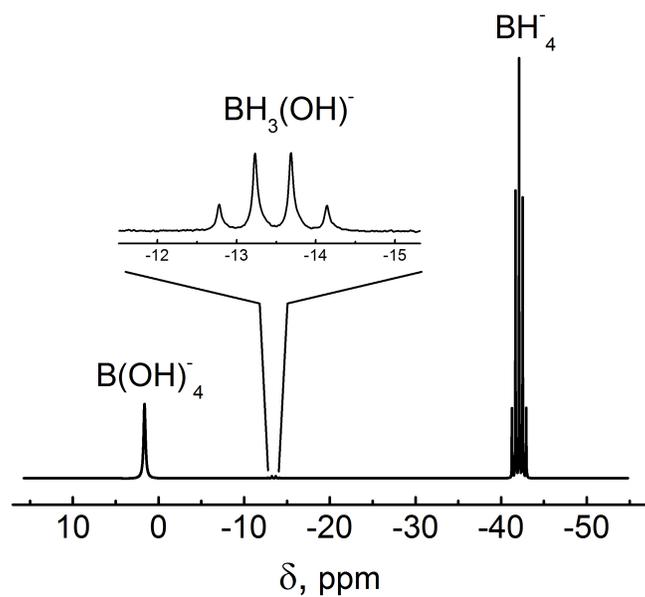


Figure 7: Proton coupled ^{11}B NMR spectrum of the aqueous NaBH_4 . The singlet at 1.6 ppm is associated to NaB(OH)_4 while the quintet at -42.1 ppm refers to BH_4^- . The J_{BH} spin-spin coupling constant for BH_4^- equals 80.6 Hz, in agreement with previous work.¹⁶ The small signal at -13.5 ppm (J_{BH} spin-spin coupling constant equal to 87.5 Hz) can be assigned to the intermediate BH_3OH^- .

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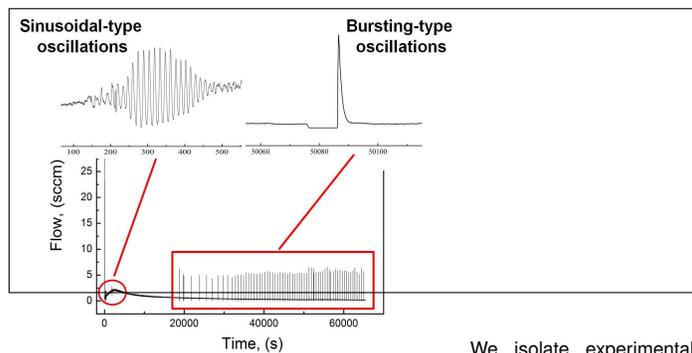
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380 **Graphical TOC Entry**

381



We isolate experimental conditions for the onset of bursting-type oscillations in the out-flow of gaseous H_2 from $NaBH_4$ hydrolysis. A minimal kinetic model for justifying the onset of an oscillatory instability in this system is also presented.