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TECHNICAL NOTE

Electrosynthesis attempts of tetrahydridoborates

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1. Introduction

Tetrahydridoborates (i.e., commonly but less accurately called borohydrides, BH_4^-) are versatile reducing agents in various organic and inorganic processes [1]. The most important manufacturing technology of $NaBH_4$ is based on the reaction of trimethyl borate $B(OCH_3)_3$, with sodium hydride at about 250 °C [2]. Electrosynthesis has been examined as a potentially simpler process for production of $NaBH_4$ and a number of patents were granted in the period 1958–1990 [3–6]. The 1958 patent by Huff and Adams [3] is rather an electrochemical metathesis reaction where the sodium from sodium borohydride is replacesd in nonaqueous media (e.g., methylamine) by another metal (e.g., Mg or Ca) which represents the sacrificial anode of the electrochemical cell. However, the rest of the patents [4–6] claim the possibility of the electrochemical reduction of both alkali metal [4, 6] and organic borates [5, 6] to the corresponding borohydrides.

The patent by Cooper [4] suggests an aqueous catholyte composed of at least 1% by weight sodium or potassium metaborate (BO_2^-). According to the patent [4] the cathode material should be either an effective hydrogenation catalyst (e.g., nickel, nickel boride, Raney nickel, platinum, cobalt, cobalt boride) or mercury. The recommended anolyte was sodium hydroxide which was separated from the cathode compartment by a cation exchange membrane. By employing cathode current densities between 0.6 and 1.5 kA m^{-2} a conversion to $NaBH_4$ of 20 to 80% was claimed [4].

More recently Sharifian together with Dutcher [5] and Hale [6], respectively, extended the patent by Cooper to produce a variety of organic quaternary ammonium and phosphonium borohydrides (i.e., $(R_1R_2R_3R_4)N^+BH_4^-$ and $(R_1R_2R_3R_4)P^+BH_4^-$, where $R_{1\ldots4}$ can be alkyl, hydroxyalkyl or alkoxyl groups). The above authors suggest as starting compounds a number of boron oxides, such as metaborates, tetraborates ($B_4O_9^{2-}$) or perborates (BO_3^-). A current efficiency for sodium borohydride of 20% was claimed after a 2 h electroreduction at 0.5 kA m^{-2} on a nickel cathode when the catholyte was composed of 10% by weight $NaBO_2$ in 1 M NaOH [6]. In a similar experiment a 25% current efficiency for tetramethylammonium borohydride was achieved.

In spite of the industrial significance of borohydrides and the potential simplicity of the electrochemical route as compared with the chemical synthesis, there is little information in the open literature regarding the electroreduction of borates to borohydrides. Generally speaking the electrochemistry of boron compounds is largely based on electrooxidations [7]. However, in a paper devoted to the voltammetric determination of BH_4^-, Mirkin and Bard briefly mentioned the complete absence of borohydride during the electroreduction of sodium metaborate [8].

The aim of the present study was to verify the above patents and to ascertain the possibility of borohydride electrosynthesis under diverse experimental conditions.

2. Experimental apparatus and procedures

2.1. *Analysis of borohydrides*

In order to avoid erroneous results leading to false conclusions, each sample was analysed by two or three different methods. Moreover, samples from blank experiments (i.e., either without current or borate) were taken and analysed to filter out possible interferences in the analytical procedure. The following methods of borohydride analysis were employed:

(i) The iodate method [9], which is based on the reaction of BH_4^- with IO_3^- followed by backtitration of the remaining IO_3^- with the I^-/I_2–$S_2O_3^{2-}$ system.
(ii) The semiquantitative silver–ethylenediamine (Ag–EDA) method [10, 11]. This method is based on the reduction of Ag(I) by BH_4^- in a 50% NaOH, 4% EDA solution. It was found to be a very convenient spot test for BH_4^- even for the nonaqueous samples analysed in the present work.
(iii) The crystal violet method [10] which was useful for nonaqueous samples.
(iv) In addition to the above analytical techniques, a new spot test was developed based on the reduction of phosphotungstate ($PW_{12}O_{40}^{3-}$) by BH_4^-. It is well known that the Keggin type anions (e.g., $PW_{12}O_{40}^{3-}$) can be easily and reversibly reduced to blue–violet species, called heteropoly blues [12]. This reaction was exploited to form the basis of a convenient and simple test for BH_4^- detection.

The following procedure was developed: to an alkaline sample containing milligram amounts of BH_4^-, about 0.2–0.3 g of phosphotungstic acid ($H_3PW_{12}O_{40}$, Aldrich Inc.) was added. The flask was swirled for about a minute followed by neutralization of the sample with H_2SO_4 0.5 M. The neutral solution exhibited the characteristic blue–violet colour of the heteropoly blue species formed by the BH_4^- reduction of $PW_{12}O_{40}^{3-}$.

The absorbance spectrum of the neutralized sample (Fig. 1) was recorded in the range of 400 to 900 nm (scanning interval 1nm). A Novaspec spectrophotometer was employed (Pharmacia Biotech) together with quartz Suprasil cuves (employable wavelength range 200–2500 nm) (Fisher Scientific Inc.). Distilled water was used as reference. A computerized peak search (Novascan Software) performed on the absorbance spectra given in Fig. 1, revealed the absorbance maximum occurring at 680 nm. The lowest BH_4^- concentration which could be detected by the above method was 10^{-4} M.

The heteropoly blue species can be reoxidized by the oxygen present in the air to the colorless phosphotungstate form. Therefore, if the sample is not completely deoxygenated, the absorbance at 680 nm is decreasing with time, making the quantitative, spectrophotometric determination of BH_4^- impossible by the phosphotungstate method.

2.2. *Electrodes, electrolytes and apparatus employed for the electroreduction of borates*

The electroreduction of borates was studied on plate and fixed-bed cathodes in both aqueous and organic media.

In aqueous media the following cathode plates were used: nickel ($A = 8.2\,cm^2$), amalgamated copper ($A = 4.3\,cm^2$), palladium ($A = 4.6\,cm^2$), zinc ($A = 5.7\,cm^2$) and Raney–Ni electroplated on a stainless steel (316) screen (superficial area $6.3\,cm^2$). The Raney–Ni was purchased from Aldrich Inc. as a 50% slurry in water with a pore size of $\sim 50\,\mu$ and a specific surface area of 80–100 $m^2\,g^{-1}$. The electroplating of Raney–Ni on the stainless steel screen was performed according to the method described by Belot *et al.* [13]. The electroplated Raney–Ni electrode was activated before each run in 4 M NaOH.

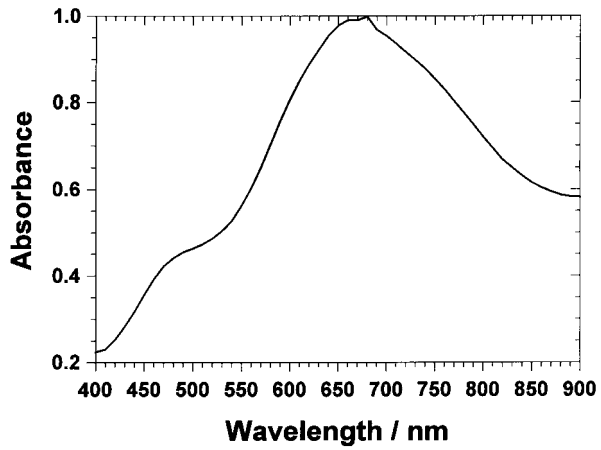

Fig. 1. Absorbance spectra of the heteropoly blue species resulted from the borohydride reduction of phosphotungstic acid. pH 7.

The nickel plate cathode was electropolished before each run by anodically polarizing it in 60% H_3PO_4 for 2 min at 1 kA m^{-2} followed by sonication in distilled water and methanol, respectively.

Additionally, in aqueous media two types of porous cathodes were tested, i.e. Raney–Ni (see above) and nickel boride (NiB, ~35 mesh, 99% purity from Cerac Inc.). The Raney–Ni was pretreated (activated) before each run by digesting it in 4 M NaOH at 60 °C for 30 min [14].

The aqueous catholyte was a NaOH solution (0.1–3 M) containing various concentrations of different borate compounds such as $NaBO_2$ (Aldrich Inc.), H_3BO_3 (BDH Inc.) or borax ($Na_2B_4O_7.10H_2O$ Aldrich Inc.).

The anode was a Pt mesh and the anolyte 1M NaOH.

In organic media either a graphite rod ($A = 3.3\,cm^2$) or an aluminum plate ($A = 5.1\,cm^2$) were employed as cathode. The catholyte consisted of trimethylborate ($B(OCH_3)_3$, Aldrich Inc.) dissolved either in ethylenediamine (Aldrich Inc.) or in a mixture of hexamethylphosphoramide (Aldrich Inc.) and ethanol. As supporting electrolyte in organic media, either lithium chloride or lithium perchlorate were used. The anolyte was 5 M LiOH and the anode a cylindrical Pt mesh.

For the cathode plates the experimental apparatus was an 'H'-cell equipped with a cation exchange membrane (Nafion® 324). The total catholyte volume was 150 ml.

For the porous cathodes the fixed-bed cell presented in Fig. 2 was used. As can be seen from Fig. 2 the basic framework of this cell is a glass funnel with a porous frit (total volume 60 ml, Pyrex®). The current feeder to the porous cathode was a circular Ni plate ($d = 4\,cm$) with a Ni wire ($d = 0.05\,cm$) welded to it. The porous cathode material (i.e., Raney–Ni or NiB) was placed on the circular Ni current feeder up to a thickness between 5 and 7 mm (superficial area $12.6\,cm^2$). The cathode compartment was separated from the anode compartment by a fine porosity ceramic frit. As anode a stainless steel (316) rod was employed.

The 'funnel' electrochemical cell (Fig. 2) provided a convenient solution for washing and rejuvenating (activating) the porous cathodes without removing the fine particles from the cell.

The reference electrode for the aqueous media experiments was a double junction saturated calomel electrode.

All experiments were performed at room temperature.

3. Results and discussion

The theoretical equation of metaborate (BO_2^-) reduction to BH_4^- in alkaline media is [15]:

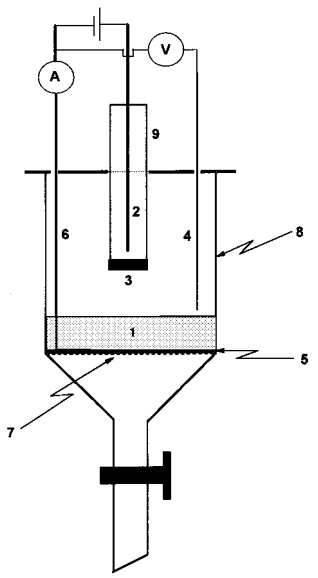

Fig. 2. The fixed-bed, 'funnel' batch electrochemical cell. Legend: (1) porous cathode, (2) anode, (3) separator (porous plug or cation exchange membrane), (4) reference electrode (SCE), (5) cathode feeder plate, (6) cathode feeder rod, (7) porous plug, (8) glass funnel, (9) glass tube.

$$BO_2^- + 6\,H_2O + 8\,e^- \longrightarrow BH_4^- + 8\,OH^- \qquad E^\circ = -1.24\,V \text{ vs SHE} \qquad (1)$$

In attempts to obtain the electrochemical reaction given by Equation 1 two experimental strategies were tested as follows: 'indirect' electrocatalytic hydrogenation of metaborate and the 'direct' electroreduction of metaborate in alkaline media. Additionally, the electroreduction of a boron compound in organic media was investigated.

3.1. *'Indirect' electrocatalytic hydrogenation*

This approach is based on the electroreduction of BO_2^- in alkaline media on electrode materials which are hydrogenation catalysts, such as Ni, Raney–Ni, NiB, palladium and zinc. These experiments followed closely the experimental conditions indicated by the patent literature [6]. Hale and Sharifian proposed the following mechanism for the electrochemical generation of BH_4^- [6]:

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^- \qquad (1)$$

$$BO_2^- + 4\,H_2 \longrightarrow BH_4^- + 2\,H_2O \qquad (2)$$

The experiments performed are summarized in Table 1. By employing several analytical methods and performing 'blank' experiments (Section 2.2) it was found that none of the experiments presented in Table 1, yielded any detectable amount of BH_4^-. Furthermore, it was observed that when the Raney–Ni bed was brought into contact with an alkaline $NaBH_4$ solution, strong hydrogen evolution occurred. This indicates that the unpolarized Raney–Ni catalyses the BH_4^- decomposition [16], therefore it cannot be employed as cathode for BH_4^- electrosynthesis. However, the same phenomena was not observed on NiB.

The iodate method of BH_4^- analysis (Section 2.2) was found to be unreliable, giving erroneously high borohydride concentrations. One of the reasons might be the insufficient acidification of the highly alkaline sample (e.g., 10% by weight $NaBO_2$ in 1 M NaOH). If the iodine titration with thiosulfate is performed at a pH insufficiently acidic (e.g., the pH is greater than 5 for a 10^{-3} N I_2 solution [17]), IO^- is generated as an intermediate and eight times less thiosulfate is consumed per one mole of iodine according to the following stoichiometry [17]:

$$S_2O_3^{2-} + 4\,I_2 + 10\,OH^- \rightarrow 2\,SO_4^{2-} + 8\,I^- + 5\,H_2O \qquad (3)$$

instead of the usual reaction

$$2\,S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\,I^- \qquad (4)$$

Thus, being a backtitration, the less thiosulfate consumed can be wrongly interpreted as a certain borohydride concentration. Furthermore, even in the case of sufficient acidification, the iodate method of BH_4^- analysis failed for samples taken from the Raney–Ni and NiB fixed bed experiments (Table 1). A black precipitate formed when KI was added to the sample. The black precipitate rendered the thiosulfate titration extremely inaccurate.

Because the electrocatalytic hydrogenation attempts of $NaBO_2$ (Table 1) yielded no detectable amount of BH_4^-, a number of experiments were performed where the electrocatalytic hydrogen evolution

Table 1. Experimental conditions for the attempted electrocatalytic hydrogenation of borates

No.	*Cathode*	*Catholyte*	*Superficial current density* /kA m^{-2}	*Cathode potential* /V vs SCE	*Reaction time* /h
1	Ni	10 wt % $NaBO_2$, 1 M NaOH	0.50	−1.20 to −1.30	1
2	Raney–Ni electrodeposited on stainless-steel screen	*ibid.*	1.34	−1.30	3
3	Raney–Ni bed	10 wt % $NaBO_2$, 1 M NaOH	1.60	−1.43 to −1.58	1
		ibid.	3.50	−2.10	
4	NiB bed	10 wt % $NaBO_2$, 1 M NaOH	1.40	−1.70 to −2.12	3
5	Pd	10 wt % $Na_2B_4O_7.10H_2O$	0.10	−1.57 to −1.63	2
6	Zn	5 wt % $NaBO_2$, 50 wt % K_2CO_3	3.5	–	2

Table 2. Experimental conditions for the attempted 'direct' electroreduction of borates

No.	*Cathode*	*Catholyte*	*Superficial current density* /kA m^{-2}	*Cathode potential* /V vs SCE	*Reaction time*/h
1	Amalgamated Cu	10 wt % $NaBO_2$, 0.1 M NaOH	0.65	−2.18 to −2.26	1
2	Amalgamated Cu	10 wt % $NaBO_2$, 2 M NaOH in TEAH*	7.50	−3.21 to −3.42	0.5
		5 wt % $NaBO_2$, in TEAH	2.44	−2.87 to −3.12	
3	Ni	20 wt % $NaBO_2$, 1 M NaOH, 0.1 M CTAB**	0.28	−1.35 to −1.41	1
4	Ni	10 wt % $NaBO_2$, 0.2 g dm^{-3} thiourea	0.50	−1.60 to −1.70	2
5	Raney–Ni electrodeposited on stainless-steel screen	1.25 wt % H_3BO_3, 1 M NaOH, 4 wt % $(CH_3)_4NI$	1.60	−1.35 to −1.40	3
6	NiB bed	*ibid.*	0.12	−1.30	4
7	Pd	10 wt % $NaBO_2$, 3 M NaOH, 0.2 g dm^{-3} thiourea	4.40	−1.90 to −2.01	1
8	Zn	10 wt % $NaBO_2$, 50 % K_2CO_3, 0.2 g dm^{-3} thiourea	3.50	−2.67 to −2.87	1

* -tetraethylammonium hydroxide 35 wt % solution in water.
** -cethyltrimethylammonium bromide.

was minimized in order to investigate the possibility of a direct electrochemical reduction of borates to BH_4^-.

3.2. *'Direct' electroreduction of borates in alkaline media*

These experiments aimed at the suppression of the electrocatalytic hydrogen evolution, thereby 'forcing' the possibility of a direct borate electroreduction.

To increase the hydrogen evolution overpotential, besides selecting appropriate cathode materials such as amalgamated copper, certain additives (i.e., quaternaryammonium compounds and thiourea) were employed as well. Thiourea increases the hydrogen evolution overpotential by retarding the recombination of the H atoms on the cathode surface [18–21]. As a consequence, strong H adsorption and surface hydride formation occurs on cathodes such as Ni, Ni alloys and Pd [20, 22]. Quaternary ammonium salts on the other hand, inhibit the electrochemical step of the hydrogen evolution mechanism [18, 21].

The experimental conditions are summarized in Table 2. Although significant overpotentials vs. the BO_2^-/BH_4^- standard potential were obtained in the presence of additives (e.g., entry no. 2, 7 and 8 in Table 2), none of the experiments presented in Table 2 gave any detectable amount of BH_4^-.

3.3. *Electroreduction of a borate ester in organic media*

Since the BH_4^- electrosynthesis attempts in alkaline aquous media were unsuccessful, the reduction of a borate ester (i.e., trimethyl borate) in organic media was investigated.

One of the most extreme reductions that one can perform is based on the so-called 'solvated' electrons [23, 24]. In this procedure the commonly employed catholyte is either the hexamethylphosphoramide (HMPA)–ethanol mixture or certain amines (e.g., ethylenediamine, EDA [25]). Lithium salts (e.g., chloride or perchlorate) are the usual supporting electrolyte in these systems.

Two experiments were performed under the above conditions with graphite and aluminum cathodes (Table 3). There were no reducing species detected in either of the two experiments.

4. Conclusions

There are a number of patents indicating the possibility of electroreduction of borate compounds to BH_4^- with 20–25% current efficiency and 20 to 80%

Table 3. Experimental conditions for the attempted electroreduction of borates in organic media

No.	*Cathode*	*Catholyte*	*Superficial current density* /kA m^{-2}	*Cell voltage* /V	*Reaction time*/h
1	Graphite	0.44 M $B(OCH_3)_3$, $1/2_{(mole/mole)}$ HMPA*/ ethanol, 0.1 M $LiClO_4$	0.08	50	3
2	Al	1.32 M $B(OCH_3)_3$, 0.5 M LiCl, 0.1 M TBAHFP†, in EDA‡	0.09	30	2

* HMPA – hexamethylphosphortriamide.
† TBAHFP – tetrabutylammonium hexafluorophosphate.
‡ EDA – ethylenediamine.

yield on electrocatalytic hydrogenation cathodes [4–6]. In spite of the claims of the patent literature, our experiments aimed at the electroreduction of borates under both electrocatalytic hydrogenation and direct electroreduction conditions in alkaline media, did not produce measurable amounts of BH_4^-. Also, attempts at the electroreduction of trimethyl borate under 'solvated electron' conditions generated no reducing species.

The commonly employed iodate method of BH_4^- analysis yielded false results in several cases. A new spot test for BH_4^- detection was developed based on the reduction of phosphotungstic acid yielding the corresponding 'heteropoly blue' species (absorbance maximum at 680 nm).

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