Sodium borohydride (BH, NaBH₄) possesses moderate reducing abilities, and is the most widely used reducing agent in chemical industry.¹ However, certain applications call for reducing powers greater than NaBH₄ (such as Superhydride, Li₃BH), while others require the reducing powers to be attenuated (such as sodium cyanoborohydride, NaBH₂CN).² Organic chemists have successfully tuned the reducing power of NaBH₄ by attaching organic electron donating or withdrawing groups to the boron center, which can also drive regio- and stereoselectivity. Judicious choice of reducing agent allows for selective reduction of the desired functional group in the presence of other reducible functional groups.

Organoborohydrides (OGBs) are typically used as stoichiometric reagents, but in the past decade, chemists have demonstrated the potential for catalytic hydrogenation using frustrated Lewis pair systems that rely on OGBs as the active reducing agent.³ The reducing power and steric bulk of these systems is carefully tuned by the organic groups attached to the boron center.

Additionally, OGBs have been investigated as potential hydrogen fuel carriers.⁴,⁵ The energy applications of the smaller NaBH₄ have been well-known for some time, both as a hydrogen carrier or as energy carrier, i.e., working as a liquid fuel (in alkaline solution) to directly feed a direct borohydride fuel cell (DBFC).⁵ In fact, the DBFC is recognized as a suitable device to power portable and mobile applications. It has higher theoretical cell voltage (1.64 V), higher than most fuel cell prototypes.⁷,⁸ Furthermore, the typical borohydride (BH₄⁻) oxidation reaction (BOR) can generate up to eight electrons per mole of NaBH₄ (Eq. 1).

\[
\text{BH}_4^- + 8\text{OH}^- \rightarrow \text{B(OH)}_4^- + 4\text{H}_2\text{O} + 8\text{e}^-
\]

\[E^0 = -1.24 \text{ V vs. SHE}\]  \[\text{(1)}\]

This eight-electron transfer mechanism is mainly obtained for gold (Au) electrodes, whereas in case of platinum (Pt) lower coulombic numbers can be achieved, with faster kinetics than Au.⁹⁻¹² Although the BH₄⁻ oxidation in alkaline aqueous solutions is a frequently discussed topic, there are still very few studies devoted to BOR in non-aqueous systems. Finkelstein et al. investigated the oxidation of BH₄⁻ in different organic media, including dimethylsulfoxide (DMSO), dimethylformamide (DMF), acetonitrile, tetrahydrofuran diglyme, methanol, ethanol, isopropanol, 1-propanol, and ether. Most solvents led to severe complications, with only DMSO and DMF demonstrating ability to avoid the BH₄⁻ decomposition to H₂ for Pt and Au electrodes.¹³ In fact, the selection of the right solvent is even more important when working with OGBs, as their solubility and stability depend on the organic solvent properties (e.g., polarity, acidity, and compatible reactivity).²

Considering that OGB compounds may also have considerable impact in energy applications, it is crucial to investigate the effects of attached organic groups on the electrochemistry of the borohydride center, as it could provide insight for chemists seeking to synthesize small molecule hydrogen carriers. Computational methods have recently established the tuning power of different organic substituents on the hydricity of the boron center, but experimentally quantifying reducing power remains difficult.¹⁴

In this work, sodium benzyloborohydride (NaC₇H₇BH₃), sodium phenylborohydride (NaC₆H₅BH₃) and sodium 4-chlorophenylborohydride (NaC₆H₄BH₃Cl) were synthesized and tested in an attempt to quantitify reducing power using electrochemical methods and to elucidate the relationship between organic tuning group and reducing ability. The prepared OGBs were characterized by ¹H and ¹³B nuclear magnetic resonance (NMR) and by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Linear scan voltammetry and chronoamperometry were used to study the OGBs electrooxidation in DMSO solutions at Au and Pt electrodes and the results are compared with those obtained for NaBH₄.

**Experimental**

**Preparation of the organoborohydride compounds.**—In this work, sodium benzyloborohydride (BBH), sodium phenylborohydride (PBH) and sodium 4-chlorophenylborohydride (CPBH) were prepared by reduction of their respective potassium organotrifluoroborates.¹⁵ Purity of >95% was confirmed by ¹H and ¹³B NMR. ¹H and ¹³B NMR spectra were recorded on a Varian Oxford AS500 spectrometer (500 MHz). ¹³B NMR chemical shifts are externally referenced to BF₃ · OEt₂ (δ 0). ATR-FTIR spectra were recorded on a Perkin-Elmer Spectrum Two spectrometer.

**Sodium benzyloborohydride.**—¹H NMR (DMSO-d₆, 500 MHz) δ 6.93 (m, 4H), 6.69 (m, 1H), 1.51 (m, 2H), 0.58 (m, 3H); ¹³B NMR

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were then converted to RHE scale by using the expression
\[ \text{ERHE} = \text{ESCE} + 0.37 \] for BH, BBH, PBH and CPBH systems, respectively. Potential values were converted to the SCE scale by adding HI (412) was done experimentally, thus potential values were converted to the reversible hydrogen electrode (RHE) scale. Namely, conversion between Au pseudo reference electrode and then converted to the reversible hydrogen electrode (RHE) scale. All potentials in the study were measured vs Au pseudo reference and a saturated calomel electrode (SCE, Hanna Instruments, HI2020 pH meter) with a Pt coil served as counter electrode and an Au disk was used as a pseudo reference electrode. The distance between the working and the reference electrodes was minimized to reduce the ohmic drop. Diffusion coefficient measurements were performed with a Pt disk microelectrode (ALS Japan, 4.91 \times 10^{-6} \text{ cm}^2) by using this small-size electrode it was possible to decrease its double-layer capacitance, thus further reducing the ohmic drop. Linear scan voltammetry was carried out at potential scan rates ranging from 5 to 200 mV s^{-1} and chronoamperometry was done at 1.5 V vs RHE, in the 25–65°C temperature range. All potentials in the study were measured vs Au pseudo reference electrode and then converted to the reversible hydrogen electrode (RHE) scale. Namely, conversion between Au pseudo reference and a saturated calomel electrode (SCE, Hanna Instruments, HI5412) was done experimentally, thus potential values were converted to the SCE scale by adding -0.37, -0.20, -0.19 and -0.14 V for BH, BBH, PBH and CPBH systems, respectively. Potential values were then converted to RHE scale by using the expression \[ \text{ERHE} = \text{ESCE} + 0.241 + 0.059 \times \text{pH (V)}, \] where the pH (10.7) was determined by a Hanna Instruments edge multiparameter HI2020 pH meter with a HI11310 pH electrode. Accordingly, all potentials given throughout the manuscript refer to the RHE reference.

**Results and Discussion**

The borohydride oxidation reaction (BOR) was initially studied at 25°C in order to estimate kinetic parameters such as the anodic charge transfer coefficient, \( \alpha \), and the number of exchanged electrons, n. Voltammograms with Pt and Au working electrodes were carried out in DMSO solutions containing 0.001 M of sodium borohydride (BH), sodium benzylborohydride (BBH), sodium phenylborohydride (PBH) or sodium 4-chlorophenylborohydride (CPBH), at potential scan rates, \( \nu \), ranging from 5 to 200 mV s^{-1} (Figure 1).

Figure 1 shows that the current densities using BH are at least twice as high as those obtained with the BBH, PBH and CPBH OGBs. Still, these BH oxidation currents obtained in organic medium are significantly lower than those generally obtained in BH aqueous solutions with the same BH concentration. Finkelstein et al. suggested that the addition of methanol to DMSO could provide methoxy ligands to stabilize the BH oxidized state, but they observed no enhancement of the anodic currents.

As expected for oxidation processes, an increase of the peak current density, \( J_p \), is observed for higher potential scan rates, \( \nu \). The peak potential, \( E_p \), is also shifted to more positive values, with no significant change of the curve shape. Thus, BOR was considered to be an irreversible single-step reaction at the studied electrodes. Therefore, the number of exchanged electrons, n, in the oxidation reaction may be calculated from the slope of the \( J_p \) vs \( \nu^{1/2} \) plots (Figure 2), by applying the Randles-Sevcik equation for irreversible processes...
Figure 2. Peak analysis as a function of \( \nu \) for Pt and Au electrodes in 0.001 M solutions of BH (a,b), BBH (c,d), PBH (e,f) and CPBH (g,h) in DMSO.

\[
j_p = 2.99 \times 10^3 (a n_a)^{1/2} n C_0 (D \nu)^{1/2} \quad [2]
\]

where \( n_a \) is the number of electrons transferred in the rate determining step (most likely 1 in this case), \( C_0 \) is the borohydride bulk concentration (mol cm\(^{-3}\)) and \( D \) is the respective diffusion coefficient (cm\(^2\) s\(^{-1}\)) in DMSO solution. While most of the \( j_p \) values (used to plot Figure 2) could be directly taken from the curves in Figure 1, for some of the higher \( \nu \) voltammograms the peak value was not so clear, as it did not correspond to a current maximum. For those situations, the trend of the \( E_p \) shift with \( \nu \) was followed to determine the corresponding \( E_p \) in the higher \( \nu \) curve. The current density was then taken at that potential value, corresponding to \( j_p \), with the method proving to be robust and reliable.

As for the \( \alpha \) coefficient, it was determined from the slope of the \( E_p \) vs. \( \ln \nu \) plots (Figure 2) using Eq. 3. \(^{10}\)

\[
E_p = E^0 + \frac{RT}{n a F} \left[ 0.78 + \ln \left( \frac{D^{1/2}}{k_s} \right) + \ln \left( \frac{a n_a F V}{RT} \right)^{1/2} \right] \quad [3]
\]

where \( E^0 \) is the formal potential (V), \( R \) is the universal gas constant (J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the temperature (K), \( F \) is faraday’s constant (C mol\(^{-1}\)) and \( k_s \) is the standard heterogeneous rate constant (cm s\(^{-1}\)). All the plots shown in Figure 2 have correlation coefficients \( (R^2) \) ranging between 0.960 and 0.997, demonstrating their good linearity and the accuracy of the fitting model.

The diffusion coefficient, \( D \), value required for application of Eq. 2 was calculated by recording the current, \( i \), with a Pt microelectrode as a function of time, following an applied potential of 0.89 V, 1.19 V, 1.29 V and 1.19 V for BH, BBH, PBH and CPBH, respectively (solid line in Figure 3).

The chronoamperometric (CA) response was linearized in the form of \( i / i_d \) vs. \( t^{-1/2} \) plots (dashed line in Figure 3) suitable for \( D \) calculation through application of Eq. 4. \(^{19}\)

\[
i(t) / i_d = (\pi^{1/2} / 4) a(Dt)^{1/2} + 1 \quad [4]
\]

where \( i_d \) is the limiting diffusion current (A) and \( a \) is the radius of the Pt microdisk (12.5 \( \times \) 10\(^{-4}\) cm). The estimated \( D \) values were then used in Eq. 2 for the determination of the \( n \) values. The \( D \) values and the BOR kinetic parameters calculated for the four compounds are summarized in Table I.

As shown in Table I, \( D \) values in DMSO were lower for the OGBs, with the \( D \) for BH being ca. 3 times higher. This is due to the large molecular dimensions of the OGBs, which have much lower mobility compared to the smaller BH. Additionally, the determined \( D \) values were ca. 2 orders of magnitude lower than those typically reported for BH in aqueous media. \(^{19}\) Since there is a paucity in the literature of BH studies in solvents other than water, it is not clear why the \( D \) values are unexpectedly low. Although a change in the \( D \) value is to be expected when switching from water to DMSO, \(^{20}\) considering that DMSO

| Parameter Electrode | BH | BBH | PBH | CPBH |
|---------------------|----|-----|-----|------|
| \( \alpha \)       | Pt | 0.97| 0.95| 0.96| 0.91 |
| Au                  | 0.97| 0.93| 0.88| 0.92 |
| \( n \)             | Pt | 6.6 | 3.4 | 3.2 | 1.6  |
| Au                  | 6.4 | 2.5 | 1.3 | 3.3  |
| \( D \)             |    | 2.87 \times 10^{-7} | 1.07 \times 10^{-7} | 1.08 \times 10^{-7} | 9.10 \times 10^{-8} | (cm^2 s^{-1}) |

Table I. Diffusion Coefficients and BOR Kinetic Parameters Determined at Pt and Au Electrodes for the Four Tested Borohydride Compounds.
ultimately affect the correct evaluation of the kinetic hydricity of the supporting electrolyte in order to avoid potential side effects that could hinder the ability of the OGBs to be oxidized at the electrode, therefore leading to lower n values. With the exception of CPBH, the n values evaluated with Pt electrode were always higher than those obtained when using Au. It is well known that the nature of the electrode (Pt or Au) plays an important role in the processes involved in BOR in aqueous media (e.g., the presence of coupled chemical reactions and adsorbed intermediates), directly affecting parameters like the number of transferred electrons or the heterogeneous charge transfer rate constant. However, present n values show a behavior which is different from that normally observed in aqueous media and may be attributed to the faster kinetics of BOR at Pt electrodes. In fact, Au electrodes are known to have sluggish BOR kinetics, causing the Au onset potential for BOR to be shifted to the right (more positive potentials) compared to Pt onset potentials. And despite Au is known for being less active than Pt for borohydride hydrolysis, which generally leads to higher n values for BOR in aqueous media, Finkelstein et al. have reported that Pt significantly outperforms Au for BH₄⁻ oxidation in direct borohydride fuel cells, providing similar electron recovery at much lower anode potentials. For the present case, as DMSO does not contain any protic H source, borohydride hydrolysis should not be promoted by the solvent, allowing Pt to exhibit higher coulombic efficiencies (i.e., higher n) than Au. On the other hand, it must be considered that although molecular sieves were used to dry the DMSO solvent, there is likely some minor water content in solution, due to the highly hygroscopic nature of DMSO. As the solution has a pH of 10.7, it would be possible to have partial hydrolysis of the compounds, though this was not observed by ¹H NMR studies of all the OGB compounds over several hours in DMSO d₆.

The concentration effect of the borohydride compounds in DMSO solution was also evaluated by recording linear scan voltammograms at 50 mV s⁻¹ for concentrations ranging from 0.001 to 0.010 M (Figure 4).

Figure 4. Effect of the borohydride concentration [0.001–0.010 M] in the voltammograms obtained at 50 mV s⁻¹ with Pt (left) and Au (right) electrodes in BH (a,b), BBH (c,d), PBH (e,f) and CPBH (g,h) solutions in DMSO.

The concentration effect of the borohydride concentration [0.001–0.010 M] in the voltammograms obtained at 50 mV s⁻¹ with Pt (left) and Au (right) electrodes in BH (a,b), BBH (c,d), PBH (e,f) and CPBH (g,h) solutions in DMSO.

Figure 5. Relation between the kinetic current density and borohydride concentration for Pt (a) and Au (b) electrodes.

| Borohydride | Pt Electrode | Au Electrode |
|-------------|--------------|--------------|
| BH          |              |              |
| BBH         |              |              |
| PBH         |              |              |
| CPBH        |              |              |

Table 1 also shows that the n values for BH were substantially higher than for the OGBs. The steric bulk of the aromatic group may hinder the ability of the OGBs to be oxidized at the electrode, therefore leading to lower n values. With the exception of CPBH, the n values evaluated with Pt electrode were always higher than those obtained when using Au. It is well known that the nature of the electrode (Pt or Au) plays an important role in the processes involved in BOR in aqueous media (e.g., the presence of coupled chemical reactions and adsorbed intermediates), directly affecting parameters like the number of transferred electrons or the heterogeneous charge transfer rate constant. However, present n values show a behavior which is different from that normally observed in aqueous media and may be attributed to the faster kinetics of BOR at Pt electrodes. In fact, Au electrodes are known to have sluggish BOR kinetics, causing the Au onset potential for BOR to be shifted to the right (more positive potentials) compared to Pt onset potentials. And despite Au is known for being less active than Pt for borohydride hydrolysis, which generally leads to higher n values for BOR in aqueous media, Finkelstein et al. have reported that Pt significantly outperforms Au for BH₄⁻ oxidation in direct borohydride fuel cells, providing similar electron recovery at much lower anode potentials. For the present case, as DMSO does not contain any protic H source, borohydride hydrolysis should not be promoted by the solvent, allowing Pt to exhibit higher coulombic efficiencies (i.e., higher n) than Au. On the other hand, it must be considered that although molecular sieves were used to dry the DMSO solvent, there is likely some minor water content in solution, due to the highly hygroscopic nature of DMSO. As the solution has a pH of 10.7, it would be possible to have partial hydrolysis of the borohydride compounds, though this was not observed by ¹H NMR studies of all the OGB compounds over several hours in DMSO d₆.

The concentration effect of the borohydride compounds in DMSO solution was also evaluated by recording linear scan voltammograms at 50 mV s⁻¹ for concentrations ranging from 0.001 to 0.010 M (Figure 4).

The BOR reaction order of the four different borohydride compounds was estimated using Eq. 5:

\[ j_0 = zC^\beta \]

where \( \beta \) is the reaction order, \( C \) is the borohydride concentration and \( z \) is a constant. From the slope of the ln \( j_0 \) vs. ln C plots (Figure 5), reaction order values were obtained with correlation coefficients higher than 0.98. For Pt electrode, \( \beta \) values of 0.94, 0.98, 0.94 and 1.33 were obtained for BH, BBH, PBH and CPBH, respectively. Reaction orders of 0.86, 0.99, 1.06 and 1.09 were found with Au electrode in BH, BBH, PBH and CPBH, respectively. This first order reaction has also been previously reported in alkaline NaBH₄ aqueous solutions, where BOR behaves as first order relatively to the BH₄⁻ ion. In order to obtain further information on BOR on these OGB compounds, complementary CA studies were performed. CA experiments were carried out in 0.001 M solutions of the corresponding...
borohydride compound in DMSO, at temperatures ranging from 25 to 65 °C (using 10 °C interval steps), by following the current with time after imposing a constant potential of 1.5 V.

Representative CA curves obtained with Au electrode at 25°C are shown in Figure 6a. In agreement with voltammetric data, BH species showed higher currents than those recorded for the OGBs. CA curves have the typical shape, including an initial sharp current decrease reaching a diffusion-controlled current after ca. 60 s. Figure 6b shows the current transients for PBH oxidation at Au electrode at temperatures ranging from 25 to 65 °C. It should be mentioned that no changes of the electrolytes’ color nor of the electrodes’ surface were detected after these experiments, which suggests stability of the system in the studied temperature range. Therefore, the apparent activation energies, $E_{a}^{app}$, were calculated from the current transients using the traditional Arrhenius equation (Eq. 6),

$$\ln j_{d} = \ln A_{i} - \frac{E_{a}^{app}}{RT}$$

where $A_{i}$ is the Arrhenius pre-exponential factor, and by plotting the logarithm of the diffusion-limited current density, $\ln j_{d}$, as a function of the reciprocal temperature, 1/T (Figure 6c).

From the slopes of the Arrhenius plots, calculated $E_{a}^{app}$ values for BOR at Pt electrodes were 18, 33, 29 and 33 kJ mol$^{-1}$ for BH, BBH, PBH and CPBH borohydride compounds, respectively. These BOR $E_{a}^{app}$ values are slightly higher than those reported$^{12}$ for BH, BBH, PBH and CPBH borohydride aqueous solutions with Au electrode, of ca. 11 kJ mol$^{-1}$, as expected considering the lower mass diffusion rates in DMSO. Nevertheless, the results show that BOR evaluation of OGB compounds in organic solvents can be effectively carried out, with kinetics similar to those of benchmark NaBH$_4$.

Conclusions

Sodium benzylborohydride, sodium phenylborohydride and sodium 4-chlorophenylborohydride were synthesized and characterized by NMR and ATR-FTIR. Solutions of these organoborohydride (OGB) compounds were tested in DMSO by chronoamperometry and voltammetric methods, for temperatures ranging from 25 to 65 °C, and borohydride concentrations ranging from 0.001 and 0.01 M. NaBH$_4$ solutions were also used for direct comparison purposes. Several electrode parameters, namely the number of exchanged electrons and the anodic charge transfer coefficients were calculated using Pt and Au macroelectrodes. By carrying out CA measurements with an Au micellelectrode it was possible to determine the diffusion coefficients of the OGB compounds in DMSO. Voltammetric measurements at different temperatures allowed application of the Arrhenius relation for calculation of the BOR activation energies for the four tested borohydride compounds. It was also found that the BOR behaves as a first order reaction for the four compounds. The application of electrochemical techniques to quantify the oxidation potential of the prepared OGBs was established. Further studies involving additional OGB compounds are necessary to be able to correlate the compounds structure with their reducing ability. As the overall BOR currents in DMSO were considerably lower than those typically obtained in borohydride aqueous solutions, future prospects are focused in further evaluating the effect of adding different supporting electrolytes to the DMSO, in order to enhance the OGB solutions’ conductivity.

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