

Figure 4. Histograms of methane concentrations of 656 water samples from different working areas.

degassed by ultrasonic treatment (samples 4-6) is nearly identical with the value of methane ($\delta^{13}\text{CH}_4 = -33.2\text{‰}$) used for the equilibration experiment. This suggests that ultrasonic vacuum degassing gives reliable information not only on the amount of methane in water samples but also on its carbon isotopic composition. The differences in $\delta^{13}\text{CH}_4$ values of gases released by both methods (He stripping and ultrasonic degassing) (samples 7 and 8; Table II) are explained by an

isotopic fractionation occurring when the helium stripping technique is used.

Application. The ultrasonic vacuum degassing system was used on board research vessels RV Sonne, RV Polarstern, and RV Meteor operating in various sea areas. During these cruises, 656 water samples were analyzed. The aim of this study was always to identify hydrothermally active areas by detection of methane plumes in the water column.

All data obtained by the new system are presented in histograms (Figure 4). A detailed discussion of the gas data will be presented elsewhere. The methane concentration of 15 nL of methane/L of seawater reflects the normal or slightly elevated background value similar to published data gained by helium stripping. High methane concentrations (in one case up to 31615 nL of CH_4/L) are probably due to hydrothermal input. Isotopic analysis will help to clarify whether the methane is of abiotic or biogenic origin.

LITERATURE CITED

- (1) Craig, H. *Geochim. Cosmochim. Acta* **1953**, *3*, 53-92.
- (2) Claypool, G. E.; Kaplan, I. R. *Natural Gases in Marine Sediments*; Plenum: New York, 1974; pp 99-139.
- (3) Stahl, W.; Faber, E.; Carey, B. D., Jr.; Kirksey, D. L. *AAPG Bull.* **1981**, *9*, 1543-1550.
- (4) Welhan, J. A.; Lupton, J. E. *AAPG Bull.* **1987**, *2*, 215-223.
- (5) Whiticar, M. J.; Faber, E.; Schoell, M. *Geochim. Cosmochim. Acta* **1986**, *50*, 693-709.
- (6) Horvitz, L. *AAPG Stud. Geol.* **1978**, *10*, 241-269.
- (7) Faber, E.; Schmitt, M.; Stahl, W. *Initial Reports of the Deep Sea Drilling Project*, Vol. XLII, p 2, Washington, 1978.
- (8) Faber, E.; Rehder, S.; Stahl, W. *Erdöl, Kohle, Erdgas, Petrochem.* **1983**, *8*, 357-361.
- (9) Horibe, Y.; Kim, K. R.; Craig, H. *Nature* **1986**, *324*, 131-133.
- (10) Kim, K. R. Ph.D. Thesis, University of California, San Diego, 1983.
- (11) Swinnerton, J. W.; Linnenborn, J. *Gas Chromatogr.* **1967**, *5*, 570-573.
- (12) Suslick, S. K. *Ultrasound: Its Chemical, Physical and Biological Effects*; VCH Verlagsgesellschaft mbH: New York and Weinheim, 1988; pp 138-163.
- (13) Dumke, I.; Faber, E.; Poggenburg, J. *Anal. Chem.* **1989**, *61*, 2149-2154.
- (14) Cicerone, R. J.; Oremland, R. S. *Global Biogeochem. Cycles* **1988**, *2*(4), 299-327.

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Voltammetric Method for the Determination of Borohydride Concentration in Alkaline Aqueous Solutions

Michael V. Mirkin and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

INTRODUCTION

Sodium and other borohydrides have been used as the reducing agents in many inorganic (1, 2) and organic (2, 3) reactions. For carrying out these reactions, as well as in studies of methods for the synthesis of borohydride, one needs a simple, rapid, and accurate analytical method to control its concentration in a solution. None of several reported analytical procedures for borohydrides meets all of these requirements. The most accurate hydrogen evolution method (4) is quite complicated. A number of titrimetric methods (2), including the iodate method, are less accurate and are also not selective. These methods, as well as polarographic (5) and spectrophotometric (6) ones, cannot be used directly in a reaction system (for example, in an electrochemical cell) to measure continuously the borohydride concentration.

To our knowledge, no one has studied the complicated electrode reaction of borohydride oxidation by cyclic voltam-

metry. We also found no previous references to the electro-oxidation of BH_4^- ion at a gold electrode. In studying this process, we found that the linear sweep voltammograms at a gold electrode (unlike those at Ni or Pt electrodes) possess a well-defined shape suitable for analytical determinations. The high stability of the gold electrode and the very low magnitude of the background current in the potential region corresponding to borohydride oxidation lead to good precision of the analytical procedure described below.

EXPERIMENTAL SECTION

Cyclic voltammetry of aqueous sodium borohydride solutions was performed in a three-electrode cell comprising a gold working electrode in a disk form (area 0.12 cm^2), a RuO_2 (dimensionally stable) counter electrode and a saturated mercurous sulfate reference electrode (SMSE). The working electrode was polished before a series of measurements with 0.05- μm α -alumina paste (Buehler, Lake Bluff, IL). No additional polishing was done

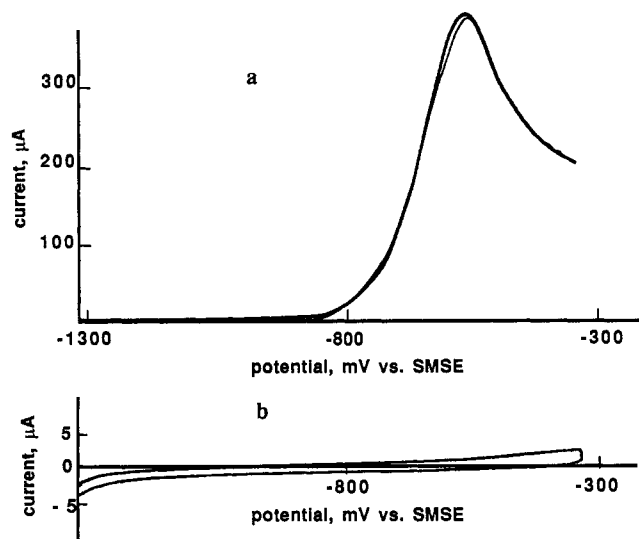


Figure 1. (a) Five successive linear sweep voltammograms of borohydride oxidation at a gold electrode obtained with time intervals of about 30 s. (b) Corresponding voltammogram of supporting electrolyte alone. Conditions: $v = 100$ mV/s, 0.2 M NaOH, 3.2 mM NaBH_4 .

between measurements in the solutions of different concentration. Voltammograms were recorded with a Princeton Applied Research (Princeton, NJ) Model 173 potentiostat.

Two series of NaBH_4 solutions with concentrations ranging from 8.1×10^{-5} to 0.013 M were prepared by diluting a 0.013 M stock solution, whose concentration was verified by the iodate method (2). The concentration of NaOH in each solution was 0.2 M; this was high enough to prevent borohydride hydrolysis (5). All chemicals were reagent grade, and water was purified by passage through a Millipore Milli-Q system. Sodium borohydride was obtained from Aldrich Chemical Co. (Milwaukee, WI).

RESULTS AND DISCUSSION

The mechanism of borohydride electrooxidation is quite complicated with the loss of up to eight electrons coupled with associated chemical reactions (5, 7). One would thus expect complicated voltammetric behavior and perhaps a dependence of $i_p/v^{1/2}$ on v (i_p , peak current; v , scan rate). For example, at a Pt electrode curves with several overlapping peaks were found. However, the voltammogram at a Au electrode consists of a single oxidation peak which possesses a well-defined shape, characteristic of an uncomplicated electrochemical process (Figure 1a). The very small background current at a gold electrode in alkaline solution in this potential region (Figure 1b) allows the use of voltammetry for low levels of BH_4^- .

The absence of any significant differences between successive voltammograms at a Au electrode suggests the absence of irreversible changes of the electrode surface in this process. However, the complexity of the electrode reaction mechanism is indicated by a nonlinear dependence of i_p on $v^{1/2}$ (Figure 2). A plot of the anodic peak current vs borohydride concentration is linear over a quite wide concentration range (Figure 3a,b). The relative standard deviation (s) of the i_p values was calculated by using five voltammograms obtained from the same solution for each concentration of BH_4^- . The maximum value of s was less than 3%. Even at a concentration of 5×10^{-5} M, subtraction of the background current was unnecessary. Only substances which can be oxidized or promote the oxidation of gold in alkaline solution in the potential region from -400 to -800 mV vs SMSE or which can adsorb onto a gold surface should interfere with this method.

This study was motivated by a possibility of electrochemical synthesis of NaBH_4 from the borate (8). In this work an important advantage of voltammetry, compared to the iodate method, is its high selectivity. The iodate method suggested erroneously high concentrations of BH_4^- in some solutions

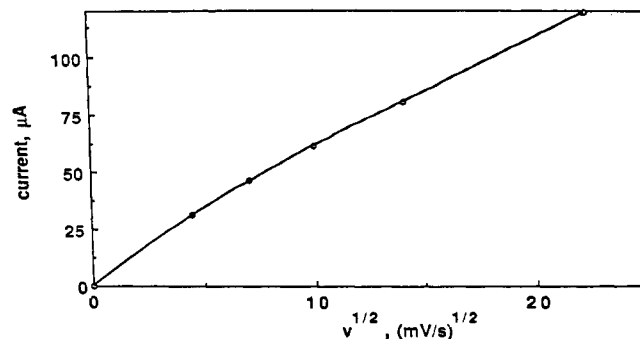


Figure 2. Dependence of a peak current on the square root of scan rate (0.2 M NaOH, 0.65 mM NaBH_4).

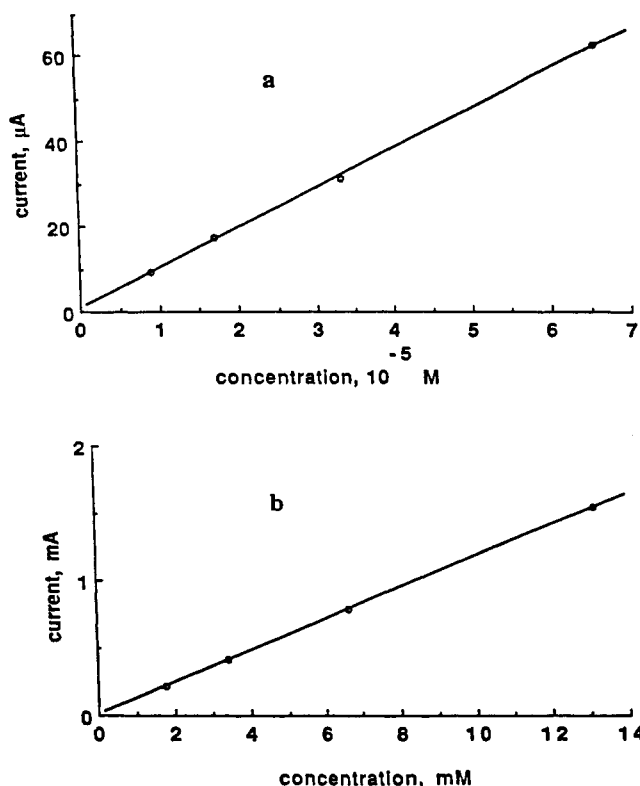


Figure 3. Dependence of peak anodic current at Au electrode on borohydride concentration. Conditions: $v = 100$ mV/s, 0.2 M NaOH.

because of other reductants produced during the electrolysis. Using the voltammetric method, we showed the absence of borohydride, even at low levels, in these solutions following electrolysis. Moreover the voltammetric method permitted the insertion of a stable gold electrode directly into the electrochemical cell during a synthesis to allow analysis during electrolysis without sampling. The voltammetric method should be similarly convenient for monitoring BH_4^- during its use as a chemical reductant in aqueous solutions.

LITERATURE CITED

- (1) Hanzlik, J. *Chem. Listy* **1973**, *67*, 1239.
- (2) *Sodium Borohydride Digest*; Morton International Inc., Specialty Chemical Group: Danvers, MA, 1989 (see also references therein).
- (3) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972.
- (4) Davis, W. D.; Mason, L. S.; Stegeman, G. J. *J. Am. Chem. Soc.* **1949**, *71*, 2775.
- (5) Gardiner, J. A.; Collat, J. W. *J. Am. Chem. Soc.* **1965**, *87*, 1692.
- (6) Lichtenstein, I. E.; Mras, J. S. *J. Franklin Inst.* **1966**, *281*, 481.
- (7) Morris, J. H.; Gysling, H. J.; Reed, D. *Chem. Rev.* **1985**, *85*, 51.
- (8) Cooper, H. B. H. U.S. Patent 3,734,842, 1973.

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