Low Level Sodium Borohydride Determination in Organic Media Using a Triarylmethyl Carbonium Ion

CYNTHIA N. RUDIE and **PAUL R. DEMKO,** Ventron Corporation, Congress Street, Beverly, MA 01915

ABSTRACT

Sodium borohydride reductions in organic solvents are used extensively for organic syntheses and for the purification of bulk organic chemicals such as alcohols, esters, amides, etc., to reduce impurities which impart color, odor, or instability to these products. A simple analytical technique based on titration has been developed to determine part per million levels of sodium borohydride in organic media.

INTRODUCTION

Sodium borohydride has achieved an increasingly important position in the chemicals industry during the past few years. It has been found effective for solving a variety of product color, odor, and stability problems. Specifically sodium borohydride has been utilized for the elimination of odor-forming impurities such as aldehydes, ketones, and peroxides in alcohols, glycols, and oxides. In detergents, amines, and amides, $NaBH_4$ has been applied to stabilize against color formation. $NaBH_4$ is also used to decolorize off-specification batches of plasticizers and as an aid in meeting low carbonyl specifications in oxo and fatty alcohols.

Typical treatment levels are in the 50-300 part per million range. There has previously been no direct analytical method for low level borohydride analysis in organic media.

The only technique available for borohydride analysis at the parts per million level is the reduction of nicotinamide adenine dinucleotide and measurement of the UV absorbance of its reduced counterpart (1). This technique requires the use of a UV spectrophotometer and is applicable only to aqueous media. Organic media must be extracted with dilute KOH solution and the extract analyzed for borohydride. In practice, this is time consuming and tedious. Described here is a simple and direct technique for estimation of borohydride content in organic media. In this method intensely colored, stable triarylmethyl carbonium ions react with hydride donors and other nucleophiles to produce colorless products. A purple solution of crystal violet in N,N dimethylformamide was employed to titrate organic solutions containing sodium borohydride to a purple endpoint. This method is simple and reasonably accurate. Quantitative results are achieved in the 1-2,000 ppm range.

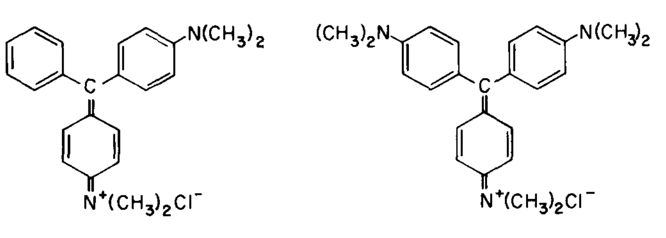

FIG. 1. Structure of malachite green and crystal violet.

EXPERIMENTAL PROCEDURES

Materials

Two triarylmethyl carbonium ions were chosen for this investigation: crystal violet (Eastman Organics) and malachite green (Eastman Organics). Commercially available materials were used without further purification. Both reagents were received as chloride salts. The structures of these carbonium ions are shown in Fig. 1. Spec. Grade DMF (Alfa Inorganics) was chosen as the solvent because $NaBH_4$ is soluble and stable in DMF. Furthermore, DMF is readily miscible with other organic media, especially higher alcohols. High purity $NaBH_4$ (Alfa Inorganics Stock No. 87658) was used for standardizing the carbonium ion solutions.

Stoichiometry Determination

The stoichiometry of the reaction between carbonium ion and borohydride was determined by titrating a known quantity of carbonium ion in DMF with borohydride in DMF. The data are summarized in Table I for crystal violet (CV^+). The equations are as follows:

$$1\ CV^+ + 1\ BH_4 \xrightarrow{DMF} CVH + \tfrac{1}{4}(BH_3)\uparrow_2$$

$$1\ MG^+ + 2NaBH_4 \text{———} MGH + (BN_3)\uparrow_2$$

TABLE I

Stoichiometry Determinations[a]

	$NaBH_4$		CV^+		Weight ratio
	ml	10^{-5}g	ml	10^{-5}g	$CV^+/NaBH_4$
I	5.00	24.5	6.60	256.1	10.45
II	8.00	39.2	10.80	419.0	10.69
III	9.95	48.8	13.70	531.6	10.89
IV	13.90	68.1	19.00	737.2	10.82
V	18.15	88.9	24.60	945.5	10.73

[a] Known concentration of $NaBH_4$/DMF was titrated with a known concentrate of carbonium ion. Concentrations:

$$NaBH_4 = 4.90 \times 10^{-5} g/ml$$

$$CV^+ = 3.88 \times 10^{-5} g/ml$$

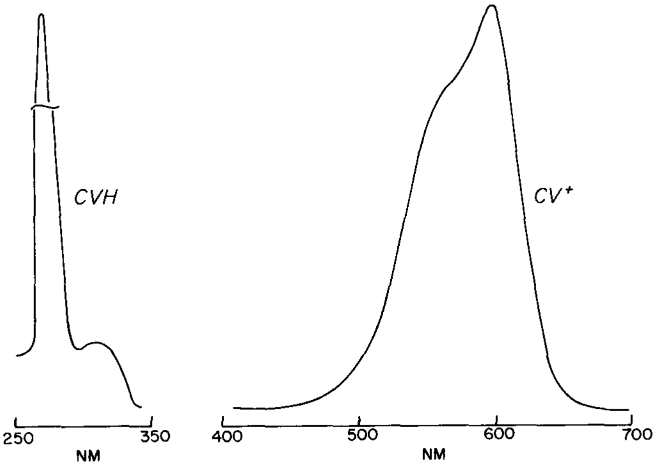

FIG. 2. UV-VIS absorption spectra of CV^+ and CVH.

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[1] Presented at 8th Northeast Regional Meeting of the American Chemical Society, Boston, MA (June 27, 1978).

TABLE II

Titration of Borohydride in Isopropanol with CV^+ DYE

$NaBH_4$ Conc. (ppm)	$CV^+/NaBH_4$	Accuracy
27	8.86	82%
54	8.80	82%
81	9.60	89%
162	10.56	98%
1,620	10.20	95%

Presumably only one hydride of each $NaBH_4$ is active due to the rapid dimerization of BH_3 to yield diborane which is evolved. The presence of diborane was qualitatively checked by adding iodine solution to the borane-containing DMF and noting that the I_2 color was discharged. There is no ready explanation for the stoichiometry observed between $NaBH_4$ and malachite green (MG^+). Therefore, further efforts were directed toward the use of crystal violet.

UV Visible Spectra

The UV-VIS Spectra of crystal violet and its reduced counterpart (CVH) were recorded using DMF as the solvent. Quartz cells were used and the spectra were recorded in nanometers on a Perkin Elmer-Hitachi 200 Spectrophotometer. Figure 2 illustrates the spectra of CV^+ and CVH.

Analysis of Sample

Solutions of $NaBH_4$ in DMF and CV^+ in DMF were prepared. Aliquots of the $NaBH_4$ solution were diluted with isopropanol to produce solutions of $NaBH_4$ in the 27 ppm to 1,620 ppm concentration range. This allowed evaluation of the accuracy of the method over a fairly wide concentration range in a typical matrix. Results are summarized in Table II.

RESULTS AND DISCUSSION

A comparison of the experimentally determined weight ratio of CV^+ to $NaBH_4$ with the theoretical value of 10.74 $CV^+/NaBH_4$ gives an indication of the accuracy of the method. All deviations from theoretical were negative. This suggests that some $NaBH_4$ may be hydrolyzed by the alcohol prior to reaction with CV^+. Table III is a compilation of matrices which have been successfully analyzed for trace quantities of $NaBH_4$ using the CV^+ in DMF titration. The accuracy of the method has been evaluated in each matrix; agreement with expected values has been within 15%.

Addition of sodium borate ($Na_2B_4O_7$) had no effect on the titration. However, addition of NaOH to CV^+ causes immediate loss of color. Strong nucleophiles are known to react with CV^+ (2) and interfere with this determination.

An example of typical application is the determination of $NaBH_4$ in n-dodecanol as follows.

Preparation and Standardization of Titrant

Crystal violet titrant is prepared by adding ~0.019 g of crystal violet dye to a 1 liter volumetric flask and diluting to the mark with DMF. A sodium borohydride standard solution is prepared by weighing 0.018 g of high purity $NaBH_4$ into a 100 ml. volumetric flask and diluting to the mark with DMF. Two milliliter aliquots of the standard borohydride solution are titrated with the crystal violet solution to a purple endpoint which persists for sixty seconds.

TABLE III

Matrices in Which CV^+ Titration Has Been Used For Analysis of $NaBH_4$ Concentrations

Solvent matrix	Applicable range ppm $NaBH_4$
EtOH	10-2,000
I-ProH	27-1,620
C_{10} Linear alcohol	6.5-127
C_{13} Linear alcohol	40-275
C_{13} Branched alcohol	40-300
C_{13} Ethoxylated alcohol	10-100
Methyl methacrylate	0-25
Ethyl acetate	0-100
Et_3N	0-100
DMF	0-2,000

$$\text{titer of } CV^+ \text{ solution in mg./ml} = \frac{\text{milligrams of } NaBH_4}{\text{milliliters of } CV^+ \text{ titrant}} = \frac{0.36 \text{ mg.}}{\text{ml. of } CV^+ \text{ titrant}}$$

Analysis

Three g of n-dodecanol are accurately weighed into an Erlenmyer flask and titrated with crystal violet solution to the same purple endpoint. The titration volume is recorded and the borohydride content is calculated as follows:

$$\text{ppm } NaBH_4 = \frac{(\text{titer of crystal violet})\ (\text{titration volume in ml})}{(\text{sample weight in grams})} \times 1{,}000$$

A spectrophotometric method employing these carbonium ions could be developed. This seems undesirable when considering that more elaborate equipment, e.g. a spectrophotometer, would be needed. The titration method is simple, rapid, and reasonably accurate.

The reliability of the method should be evaluated in each matrix to be analyzed since the matrix could consume $NaBH_4$ by hydrolysis or react with the CV^+. This can be conventiently done by preparing a series of known borohydride concentrations in a particular matrix and calculating accuracy as described in the results section.

ACKNOWLEDGMENT

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