Technical Bulletin AL-123

Quantitative Analysis of Active Metals and Metal Hydrides via Gas Buret

revised 4 / 96

4 pages

Active metals (M) and metal hydrides (MH) (including boron hydrides) react rapidly and quantitatively with suitable hydrolytic solvents to produce hydrogen gas (eqs. 1 and 2).

$$M + HOR \longrightarrow MOR + \tfrac{1}{2} H_2 \qquad \text{(eq.1)}$$

$$MH + HOR \longrightarrow MOR + H_2 \qquad \text{(eq.2)}$$

The direct measurement of the volume of hydrogen gas produced provides a convenient and highly accurate method for the determination of concenctraction or purity of these reagents. Metals and metal nydrides that can be analyzed in this manner include sodium and lithium as dispersions in mineral oil, borane-tetrahydroguran and borane-methyl sulfide complexes, 9-BBN, K-Selectride®, lithium aluminum hydride, diisobutylaluminum hydride. Several reviews regarding the use and handling of boron hydrides and other active metals and metal hydrides are available.[1-7]

A simple gas buret for measuring the volume of hydrogen gas is illustrated in Fig.1. This apparatus can be assembled from readily available laboratory equipment.

Procedures

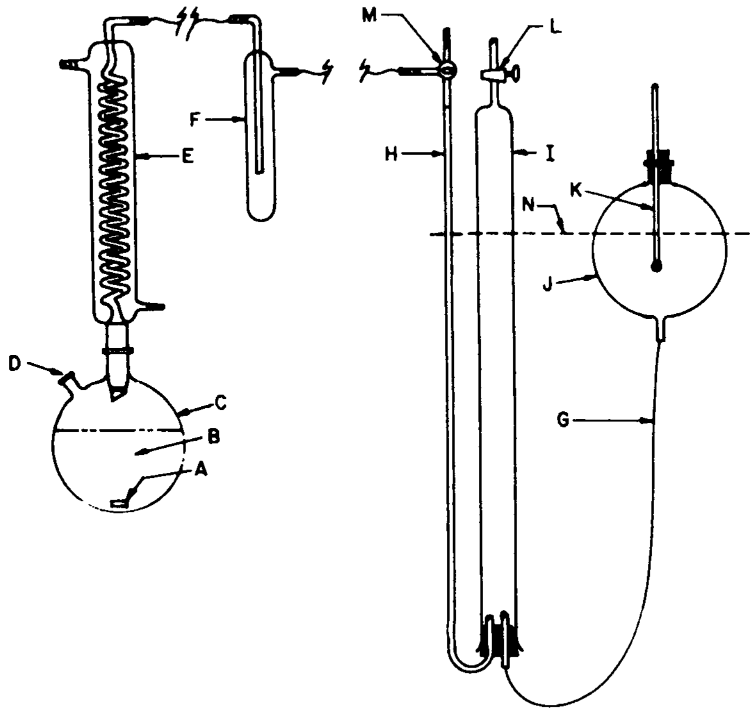
A. Determination of hydride concentration of a solution

The following procedure for determining the hydride concentration of a BH_3•THF solution is representative. The gas buret is assembled as illustrated in Fig. 1 and the hydrolysis flask **C** is charged with 50ml of glycerol and 50ml of water. Cooling water is run through the spiral condenser **E** and trap **F** is cooled in dry ice/acetone. With stopcocks **L** and **M** both open to the atmosphere, the leveling bulb **J** is adjusted to give a zero reading for the level of distilled water in the gas buret.[8] Stopcock **L** is then closed and stopcock **M** is turned so that the hydrolysis flask and the gas buret form a closed system. An accurately measured aliquot of the BH_3•THF solution (2.00ml of a 1*M* solution generates *ca.* 150ml of hydrogen) is added slowly through the septum inlet to the stirred glycerol/water solution using a hypodermic syringe.4,5 Hydrolysis of the BH_3•THF solution is extremely rapid, being complete in a few seconds.

B. Hydride determination of solid inorganic hydrides or hydrogen-generating metals

Assemble the gas buret as in Fig. 1, without the hydrolysis flask. Turn on the cooling water and cool trap **F** in a dry ice/acetone bath. With stopcocks **L** and **M** open to the atmosphere, adjust the leveling bulb **J** to give a zero reading.

Figure 1



A. Magnetic stirring bar
B. Hydrolysis solution
C. 200- to 300ml flask
D. Septum inlet
E. Sprial condenser
F. Cold trap (dry ice/acetone)
G. Flexible polyvinyl tubing
H. Heavy-wall glass tubing
I. 250ml buret
J. Leveling bulb
K. thermometer
L. 4mm straight-bore stopcock
M. 4mm T-Bore stopcock
N. Water level

Inside a glove bag and under nitrogen or argon, transfer 3-6 meq of sample to a septum-topped, flushed, tared 100ml septum-inlet-equipped flask containing a stirring bar. (An antistatic alpha-emitter plate held next to the neck of the flask during transfer controls loss of sample onto the neck of the flask.) Reseal the flask and reweigh. Working quickly, attach the sample flask in position under the condenser. Add 10ml of anhydrous solvent (which has been stored over calcium hydride) through the septum inlet **D** to slurry the solid. Close stopcock **L**; turn stopcock **M** so that the sample flask and gas buret form a closed system. Slowly inject 2.0ml of hydrolysis solution. In most cases, hydrolysis is complete in less than 2 minutes.

When hydrolysis is complete, the water level in glass tube **H** will remain constant at a level considerably below the water level in the buret. To obtain an accurate reading of the volume of hydrogen gas produced, the water level in the side tube **H** must be coplanar with the water level in the buret **I**. Consequently, more hydrogen gas must be forced over into the buret to raise the water level in the side tube until it corresponds to the water level in te buret. This is easily accomplished be quickly lowering the leveling bulb **J** to a point below the outlet of the side tube in the buret and then raising the leveling bulb to its original position. The lowering and raising of the leveling bulb are repeated until the water levels in the side tube, buret and leveling bulb are all coplanar. The final buret reading is then taken as illustrated in Fig. 1.

The analysis is reapeated until three separate analyses vary by no more than 1ml. Occasionally, the initional analysis will be highly innaccurate and this result should be discarded. When consistent measurements are obtained for the has volume, the molarity of the borane solution is calculated using the following equation:

$$\text{Borane molarity} = \frac{(P_1\text{-}P_2)\,(273)\,(V_1\text{-}V_2)}{(760)\,(T)\,(22.4)\,(V_2)\,(n)}$$

Where:

P_1 = observed pressure (mm Hg)

P_2 = vapor pressure (mm Hg) of water at T (see Table 1)

V_1 = volume (ml) of hydrogen has evolved

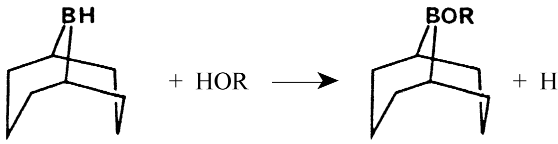
V_2 = volume (ml) of borane solution injected into hydrolyzing solution

T = observed temperature (°K)

n = number of moles of hydrogen produced per mole of sample; The value of n is 3, for example, for BH_3•THF since 3 moles of hydrogen are generated from one mole of BH_3•THF solution at standard temperature and pressure based on the stoichiometry shown in eq. 3.

$$BH_3 + 3\,HOR \longrightarrow B(OR)_3 + 3\,H_2 \qquad \text{(eq. 3)}$$

For 9-BBN, K-Selectride® and Super-Hydride®, the value of n is 1, based on the stoichoimetry shown in eqs. 4 and 5.



(eq.4)

$$M[R_3BH] + HOR' \longrightarrow MOR' + R_3B + H_2 \qquad \text{(eq.5)}$$

The procedure described for analysis of the BH_3•THF solution can be easily adapted to the analysis of solutions of other active hydrides by changing the hydrolysis solution and conditions. Table 2 is a summary of the conditions necessary for the hydrolysis of various active hydride solutions.

The activity or purity of a solid compound is calculated using the following equation:

$$\%\,MH_n\ (\text{or }\%M) = \frac{(P_1\text{-}P_2)\,(273)\,(V_1\text{-}V_3)\,(MW)\,(100)}{(760)\,(T)\,(22.4)\,(x)\,(n)}$$

Where:

V_3 = volume of hydrolyzing solution added

MW = molecular weight

x = weight of sample in mg

Table 3 is a summary of solvents and hydrolyzing solutions necessary for the hydrolysis of various solid metal hydrides and hydrogen-generating metals.

C. DETERMINATION OF PURITY OF SOLID OR LIQUID BORON HYDRIDES

The simplest procedure for solid or liquid boron hydrides involves first dissolving an accurately weighed quantity of pure boron hydride in an appropriate dry solvent (*e.g.*, THF) in a volumetric flask. Dilution to a known volume gives a standard solution. The theoretical molarity can then be calculated and compared with the experimental molarity determined by hydrogen evelution upon hydrolysis. Table 4 summarizes the conditions necessary for the hydrolysis of various solid or liquid boranes dissolved in THF.

Borane-*tert*-butylamine, borane-dimethylamine, borane-morpholine, borane-pyridine, borane-triethylamine, and borane-trimethylamine complexes are all essentially unreactive toward hydrolytic solvents at neutral pH. These amine-boranes are hydrolyzed by aqueous mineral acids (eq. 6). However, the reaction is generally too slow to be used conveniently for quantitative analysis *via* hydrogen evolution; *e.g.*, a period of 6 hours is necessary for the complete hydrolysis of borane-triethylamine by 1*M* HCl in water/ethylene glycol solution.[5] These hydrolytically stable borane complexes are more conveniently analyzed by IR, NMR, GC or elemental analysis.

$$H^+ + R_3N\bullet BH_3 + 3\,H_2O \longrightarrow R_3\overset{+}{N}H + H_3BO_3 + 3\,H_2 \qquad \text{(eq.6)}$$

Table 1

Vapor Pressure (mm Hg) of Water*

Temp. °C	0.0	0.2	0.4	0.6	0.8
19	16.477	16.685	16.894	17.105	17.319
20	17.535	17.753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20.316	20.565	20.815
23	21.068	21.324	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912

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Table 2

Conditions for the Hydrolysis of Active Metal-Hydride Solutions

Catalog No.	Description	Hydrolysis	
		Solution[a]	Rate[b]
22,902-4	**R-Alpine-Hydride®**	G-W-THF	R
23,772-8	**S-Alpine-Hydride®**	G-W-THF	R
19,385-2	**9-BBN**, 0.5*M* in hexanes	M-THF	S
15,107-6	**9-BBN**, 0.5*M* in THF	M-THF	S
25,883-0	**9-BBN-pyridine**, 0.5*M* in diethyl ether	1	R
19,211-2	**Borane-methyl sulfide complex**, 2.0*M* in diethyl ether	G-W-M	R
19,212-0	**Borane-methyl sulfide complex**, 2.0*M* in THF	G-W-M	R
19,482-4	**Borane-methyl sulfide complex**, 2.0*M* in toluene	G-W-M	R
17,619-2	**Borane-tetrahydrofuran complex**, 1.0*M* in THF	G-W	R
22,576-2	**Catecholborane**, 1.0*M* in THF	G-W-THF	R
21,494-9	**Diisobutylaluminum hydride**, 1.0*M* in cyclohexane	2	R
19,030-6	**Diisobutylaluminum hydride**, 1.0*M* in hexanes	2	R
21,497-3	**Diisobutylaluminum hydride**, 1.0*M* in dichloromethane	2	R
21,498-1	**Diisobutylaluminum hydride**, 1.0*M* in THF	2	R
21,500-7	**Diisobutylaluminum hydride**, 1.0*M* in toluene	2	R
22,076-0	**K-Selectride®**	G-W-THF	R
22,077-9	**KS-Selectride®**	G-W-THF	R
21,279-2	**Lithium aluminum hydride**, 1.0*M* in diethyl ether	3	R
23,605-5	**Lithium aluminum hydride**, 0.5*M* in diglyme	3	R
21,277-6	**Lithium aluminum hydride**, 1.0*M* in THF	3	R
24,394-9	**Lithium aluminum hydride bis(tetrahydrofuran)**, 1.0*M* in toluene	3	R
23,020-0	**Lithium borohydride**, 2.0*M* in THF	3	R
24,453-8	**Lithium thexyllimonylborohydride**, 0.5*M* in THF	G-W-THF	R
17,849-7	**L-Selectride®**	G-W-THF	R
22,592-4	**LS-Selectride®**	G-W-THF	R
21,340-3	**N-Selectride®**	G-W-THF	R
21,343-8	**Potassium triethylborohydride**, 1.0*M* in THF	G-W-THF	R
19,789-0	**Potassium triisopropoxyborohydride**, 1.0*M* in THF	G-W-THF	R
24,392-2	**1-Pyrrolylborane**, 1.0*M* in THF	G-W-THF	R
20,097-2	**Sodium borohydride**, 0.5*M* in diglyme	HCl-EG-W	R
21,551-1	**Sodium borohydride**, 2.0*M* in triglyme	HCl-EG-W	R
22,731-5	**Sodium triethylborohydride**, 1.0*M* in diethyl ether	G-W-THF	R
21,341-1	**Sodium triethylborohydride**, 1.0*M* in THF	G-W-THF	R
22,730-7	**Sodium triethylborohydride**, 1.0*M* in toluene	G-W-THF	R
18,086-6	**Super-Deuteride®**	G-W-THF	R
17,972-8	**Super-Hydride®**	G-W-THF	R

[a] Hydrolysis solutions prepared by combining equal volumes of the solvents given where G = glycerol, W = water, M = methanol, EG = ethylene glycol, THF = tetrahydrofuran and HCl = 6*M* hydrochloric acid.

[b] R = Rapid, hydrolysis complete in < 5 minutes at 20-25°. S = slow, hydrolysis requires 15-20 minutes for completion at 25°.

1 = Conc. HCl and methanol 1:1 cooled i ice bath
2 = Conc. HCl, water, hexanes 1:1:4 cooled in ice bath
3 = 2N HCl cooled in ice bath

HANDLING INSTRUCTIONS

The reagents discussed in this bulletin are air- and /or moisture sensitive. Mose of the products are supplied in our Sure/Seal™, Sure/Pac™ or Kilo-Lab™ containers for extra protection. Te products are to be handled, and the procedures outline here performed only be technically qualified persons. For information on the techniques and equipment for handling these products safely, a number of Technical Information Bulletins[4-8] is available from Aldrich. The bulletins are available free upon request.

REFERENCES AND NOTES

1• Brown, H.C.; Kramer, G.W.; Levy, A.B.; Midland, M.M. *Organic Synthesis via Boranes*; John Wiley and Sons, Inc.: New York, 1973; pp 21-244 (Aldrich Catalog No. Z10,144-3).

2• Murray,L.I. "A Study of the Amine-bornes", Ph.D. Thesis, Purdue University, Lafayette, 1963.

3• *Handling Air-Sensitive Reagents*, Aldrich Technical Information Bulletin No. AL-134.

4• *Equipment for Handling Air-Sensitive Reagents*, Aldrich Technical Information Bulletin No. AL-135.

5• *The Aldrich Sure/Pac™ Cylinder Packaging Systemand Recommended Transfer Procedures*, Aldrich Technical Information Bulletin No. AL-136.

6• *Aldrich Kilo-Lab™ Cylinder Packaging System and Recommended Transfer Procedures*, Aldrich Technical Information Bulletin No. AL-149.

7• *Equipment for Transfer of Liquids from Aldrich Kilo-Lab™ Cylinders*, Aldrich Technical Information Bulletin No. AL-150.

8• Normally, a small amount of cupric nitrate is dissolved in the water to prevent algae growth.

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TABLE 3
CONDITIONS FOR HYDROLYSIS OF SOLID METAL HYDRIDES AND ACTIVE METALS

Catalog No.	Description	Solution[a]	Solution[b]
20,802-7	**Calcium hydride**, -4+40 mesh	T	W
21,326-8	**Calcium hydride**, -40 mesh	T	W
21,332-2	**Calcium hydride**, -1+4 mish	T	W
24,881-9	**Lithium**, 25 wt % in mineral oil, high Na	THF	I-M
24,882-7	**Lithium**, 25 wt % in mineral oil, low Na	THF	I-M
19,987-7	**Lithium aluminum hydride**	T	W
20,104-9	**Lithium hydride**	T	W
21,581-3	**Potassium hydride**, 35% in mineral oil	THF	THF-W
21,712-3	**Sodium**, 40 wt % in light oil	THF	THF-W
21,711-5	**Sodium**, 40 wt % in odorless mineral spriits	THF	THF-W
19,807-2	**Sodium borohydride**	THF	HCl-EG-W
22,344-1	**Sodium hydride**	THF	I-M
19,923-0	**Sodium hydride**, 60 wt % in mineral oil	T	W
25,399-5	**Sodium hydride**, 80 wt % in mineral oil	T	W

[a] Solvent is 10ml of either toluene (T) or tetrahydrofuran (THF)

[b] Hydrolysis solution mixtures are prepared by combining equal volumes of solvents where W = water, I = isopropanol, M = methanol, HCl = 6*N* hydrochloric acid and EG = ethylene glycol

TABLE 4
CONDITIONS FOR THE HYDROLYSIS OF PURE BORON HYDRIDES

Catalog No.	Description	Solution[a]	Rate[b]
17,871-3	9-BBN	M-THF	S
17,904-3	Borane-N,N-diethylaniline	G-W-THF	S
25,311-1	Borane-N,N-diisopropylethylamine	EG-HCl	R
17,982-5	Borane-methyl sulfide	G-W-M	R
22,490-1	Borane-1,4-oxathiane	G-W-M	R
17,983-3	Borane-4-phynylmorpholine	G-W	R
17,975-2	Borane-pyridine	H_2SO_4-W-EG	R

[a] Hydrolysis solutions prepared by combining equal volumes of the solvents given; where G = glycerol, W = water, M = methanol, EG = ethylene glycol, THF = tetrahydrofuran and HCl = 6*N* hydrochloric acid

[b] R = Rapid, hydrolysis complete in < 5 minutes at 20-25°. S = Slow, hydrolysis requires 15-20minutes for completion at 25°.

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