HYDROXYALKOXYL

PRINCIPLE

Hydroxyalkoxyl groups in starch ethers are decomposed by hot, constant boiling hydroidic acid in a modified Zeisel procedure. Hydroxyethyl groups give both ethyl iodide and ethylene, hydroxypropyl groups give both propyl iodide and propylene, which are determined volumetrically with standard solutions of silver nitrate and bromine, respectively (Notes 1, 2).

SCOPE

The method is applicable to starch ethers and, in particular, to hydroxyethyl and hydroxypropyl starch ethers.

SPECIAL APPARATUS

1. Glassware: The principal glassware parts are shown in the attached drawing. The apparatus is available on special order from SGA Scientific Inc., Elk Grove Village, Illinois 60007. Not shown is the reaction flask, a 50 mL round bottom flask with attached capillary tube for introduction of the sweeping gas. This flask is a standard item and may be ordered as JM 4355, St 14/20, 50 mL flask. Standard-taper joints include a 24/25 joint for trap 1, 14/20 joints for traps 2 and 3, connecting 18/7 ball joints for traps 2 and 3, and a 24/40 joint at the bottom of trap 3.

2. Heating Bath: A bath of dimensions 6" × 6" × 4" containing silicone oil (Dow Corning 550) and equipped with a 500 watt immersion heater and thermoregulator. The bath rests on a magnetic stirrer and both bath and stirrer are attached to a Ceno-Lerner Lab-Jack for ease in raising and lowering around the reaction flask.

3. Flowmeter: A low-flow flowmeter is placed in the Tygon tubing line leading from the carbon dioxide cylinder to the side arm of the reaction flask, e.g., a Model 622PB1 flowmeter is obtainable from the Matheson Company, Inc., Joliet, Illinois 60431.

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REAGENTS

1.   Hydroidic Acid, 57%: A high purity constant boiling acid (HI) of specific gravity 1.7 must be used. This is available as Item 623, 57% Hydroidic Acid from the G. Frederick Smith Chemical Co., 867 McKinley Avenue, Columbus, Ohio 43223.

2.   Alcoholic silver Nitrate Solution: Dissolve 15 g of silver nitrate ($AgNO_3$) in 28 mL of water, add 420 mL of 95% ethyl alcohol (Formula 3A plus water) and 5 drops of concentrated nitric acid (HNO_3). Store in a brown bottle. Standardize with 0.10 N potassium thiocyanate by the Volhard method.

3.   Potassium Thiocyanate Solution, 0.10 N: Standard

4.   Ferric Alum Indicator ($FeNH_4(SO_4)_2 \bullet 12H_2O$): Saturated aqueous solution of ferric ammonium sulfate

5.   Bromine – Acetic Acid Solution: Add 1 mL bromine (Br_2) to 300 mL glacial acetic acid (CH_3COOH), previously saturated with dry potassium bromide (KB_r) (5 g). Store in a brown bottle in a dark place. Standardize with thiosulfate solution daily when in use.

6.   Sodium Thiosulfate ($Na_2S_2O_3$) 0.10 N: Standard

7.   Potassium Iodide, 10%: Aqueous solution

8.   Starch Indicator, 1%

9.   Sodium Thiosulfate-Cadmium Sulfate Solution: Mix equal volumes of a 5% aqueous solution of sodium thiosulfate ($Na_2S_2O_3$) and a 5% aqueous solution of cadmium sulfate ($CdSO_4$).

10.   Phenol: White crystals, Reagent ACS

11.   Propionic Anhydride: B.P. 165-167 °C

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12.   Nitric Acid Solution, 1 *N*:   Add 64 mL of concentrated nitric acid (70% HNO_3, sp g 1.42) to 800 mL of purified water and dilute to 1 L with purified water.

PROCEDURE

Add 10 mL of the sodium thiosulfate-cadmium sulfate solution to trap 1. Add exactly 10.0 mL alcoholic silver nitrate solution to trap 2. Remove the Widmer spiral and add, with a safety pipet, exactly 15 mL of the bromine-acetic acid solution to trap 3. Replace the widmer spiral. Add 10 mL of the 10% potassium iodide solution to trap 4. Connect all traps.

Weigh the sample into a size 000 gelatin capsule (Note 2) and place in the reaction flask. Add 1.0 g phenol, 0.5 mL propionic anhydride 2 boiling granules and 30 mL hydroidic acid. Connect the flask to the reflux column at A using several drops of hydroidic acid as a seal for the glass joint. Secure with springs.

Set the reducing valve of the carbon dioxide cylinder to 5 lbs. Gas pressure and adjust the flowmeter to give a gas flow of 1 cc per min. Connect to the reaction flask. The flow rate should be one bubble per second through trap 1.

Raise the Lab-Jack holding the heated bath, temperature 140-145 °C, until the oil level is slightly above the level of the hydroidic acid in the reaction flask. Heat for 1 to 1.5 hrs. at which time most reactions are complete. At the end of the reaction, the supernatant liquid in the silver nitrate trap becomes clear and the precipitate is well settled.

Lower the Lab-Jack until the reaction flask is completely out of the oil bath. Warm the silver nitrate trap with water at 45 °C to drive out any dissolved olefin into the bromine solution.

Remove the carbon dioxide line from the capillary of the reaction flask and slowly open the side arm stopcock on trap 2. Remove trap 4, disconnect trap 3 and attach a 250 mL iodine flask to trap 3. Wash the contents of trap 3 into the flask, add the content of trap 4, stopper the iodine flask and let stand 5 mins. Titrate with standard 0.10 *N* sodium thiosulfate solution, adding 1 mL of starch indicator when only a pale yellow color remains. Continue the titration to a colorless end point.

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Wash the contents of the alcoholic silver nitrate trap into a 250 mL iodine flask containing 50 mL of water. Add 1 mL of ferric alum indicator and 5 mL of 1 *N* nitric acid. Titrate with standard 0.10 *N* potassium thiocyanate solution to a faint pink color.

CALCULATION

Subtract the titration values for the unused silver nitrate, and bromine-acetic acid solutions from their corresponding reagent blank titrations. The reagent blank titrations are obtained using reagents and a gelatin capsule containing 0.5 g dextrose as the sample.

Calculate results on the basis of the ethylene oxide unit, C_2H_4O, molecular weight 44.05, or the propylene oxide unit, C_3H_6O, molecular weight 58.08.

Hydroxyethyl Starch

A. $\% \, C_2H_4O$ (dry basis) from C_2H_4 $= \dfrac{\text{(Net Thiosulfate Titer, mL)}(N)(92.203)(100)}{\text{(Sample Wt., g)(dry substance)}}$

B. $\% \, C_2H_4O$ (dry basis) from C_2H_5I $= \dfrac{\text{(Net Thiocyanate Titer, mL)}(N)(4.405)(100)}{\text{(Sample Wt., g)(\% dry substance)}}$

Total % C_2H_4O (dry basis) = Sum (A and B)

To calculate the molar substitution (MS) in terms of hydroxyethyl groups per anhydroglucose unit:

$$MS = \frac{\% \, C_2H_4O \text{ found} \times 162}{(100 - \% \, C_2H_4O \text{ found}) \times 44.05}$$

Hydroxypropyl Starch

A. $\% \, C_3H_6O$ (dry basis) from C_3H_6 $= \dfrac{\text{(Net Thiosulfate Titer, mL)}(N)(2.904)(100)}{\text{(Sample Wt., g)(\% dry substance)}}$

B. $\% \, C_3H_6O$ (dry basis) from C_3H_7I $= \dfrac{\text{(Net Thiocyanate Titer, mL)}(N)(5.808)(100)}{\text{(Sample Wt., g)(\% dry substance)}}$

Total % C_3H_6O (dry basis) = Sum (A and B)

To calculate the molar substitution (MS) in terms of hydroxypropyl groups per anhydroglucose unit:

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$$\text{MS} = \frac{(\% \text{ C}_3\text{H}_6\text{O found})(162)}{(100 - \% \text{ C}_3\text{H}_6\text{O found})(58.08)}$$

NOTES AND PRECAUTIONS

1. Reference supplying further information concerning reactions, applications, and interferences are: P.W. Morgan, *Ind. Eng. Chem., Anal. Ed.,18,* 500 (1946); H.J. Lortz, *Anal. Chem., 28* 892 (1956); A. N. deBelder, A. Persson, and S. Markstrom, *die Stäke, 24,* 361 (1972).

2. Modern approaches utilize the basic principle of the Zeisel hydriodic acid reaction, however, in the presence of adipic acid catalyst, which prevents the formation of alkene, so that only the alkyl iodide needs to be measured. This is done by gas chromatography of a xylene extract of the reaction mixture. The basic references are as follows:
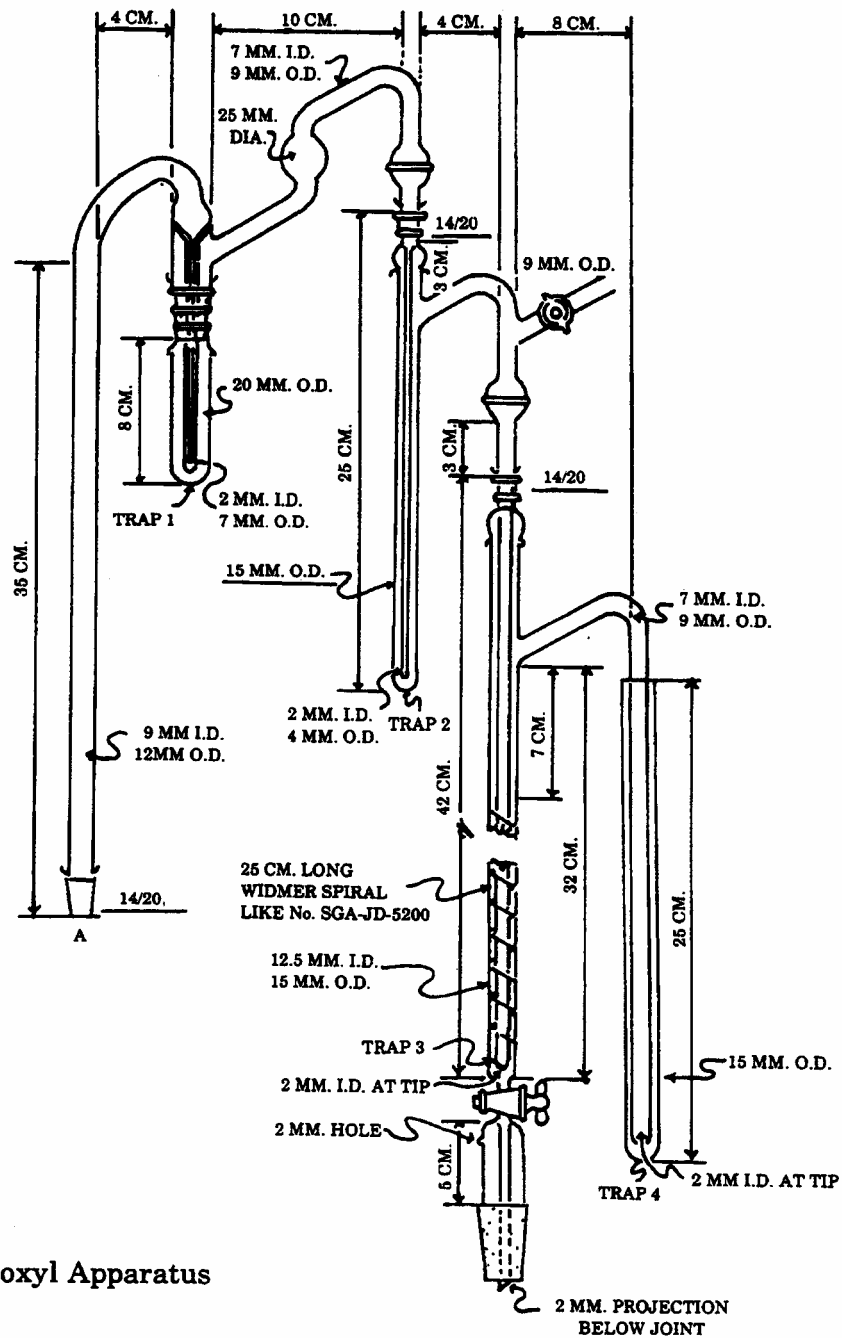
    Y. C. Lee, D. M. Baaske and J. E. Carter, Determination of the Molar Substitution Ratio of Hydroxyethyl Starches by Gas Chromatography, *Anal. Chem., 55,* (13), 334-338 (1983).

    K. L. Hodges, W. E. Kestler, D. L. Wiederrich and J. A. Grover, Determination of Alkoxy Substitution in Cellulose Ethers by Zeisel – Gas Chromatography, *Anal. Chem., 55,* (13) 2172-2176 (1979).

3. Dry samples are preferable. Use 0.8-1.0 g for starches with a $\text{C}_2\text{H}_4\text{O}$ content of 1-2%, and decrease the sample size to 0.3 g for 10% $\text{C}_2\text{H}_4\text{O}$. Samples that contain glycol residues should be well washed with water and dried prior to analysis.

METHOD HISTORY

Corn Starch (Modified), Hydroxyalkoxyl (C-30), Date of Acceptance 11-09-1973, Revised 5-19-1995.

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4 CM.   **10 CM.**   **4 CM.**   **8 CM.**

7 MM. I.D.
9 MM. O.D.

25 MM. DIA.

14/20

9 MM. O.D.

3 CM.

8 CM.

20 MM. O.D.

25 CM.

3 CM.

14/20

35 CM.

2 MM. I.D.
7 MM. O.D.

TRAP 1

15 MM. O.D.

7 MM. I.D.
9 MM. O.D.

7 CM.

9 MM I.D.
12MM O.D.

2 MM. I.D.
4 MM. O.D.

TRAP 2

42 CM.

32 CM.

25 CM.

25 CM. LONG
WIDMER SPIRAL
LIKE No. SGA-JD-5200

14/20,

A

12.5 MM. I.D.
15 MM. O.D.

TRAP 3

15 MM. O.D.

2 MM. I.D. AT TIP

2 MM. HOLE

5 CM.

2 MM I.D. AT TIP

TRAP 4

Hydroxyalkoxyl Apparatus

2 MM. PROJECTION
BELOW JOINT