Electrolysis of low molecular weight carbohydrates in non-aqueous media.[1] I. The products of electrolysis of monosaccharides

G. W. HAY[2,3,4]

Department of Chemistry, Queen's University, Kingston, Ontario

AND

F. SMITH[5]

Department of Biochemistry, College of Biological Sciences, University of Minnesota, St. Paul, Minnesota 55101

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The electrolysis of monosaccharides in alkaline, non-aqueous media caused a sequential descent of the series as a result of the elimination of one-carbon units from the reducing end of the molecule, without the formation of chromatographically detectable quantities of oxidized derivatives.

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Introduction

Since the initial detection of acids from the electrolysis of sucrose (1) and glucose (2) relatively few studies of electrochemical reactions of carbohydrates have been published. The synthetic applications other than the electrochemical synthesis of D-gluconic (3–6) and other aldonic acids (7–10), D-glucitol and D-mannitol (11, 12), and periodate oxystarch (13) remain largely unexploited.

The electrolysis of carbohydrates in aqueous solution usually involves both hydrolytic and oxidative reactions in which carbonyl (4, 14, 15) and/or carboxyl (1, 3–9, 16) groups are introduced into the parent compound. Thus, polysaccharides and proteins may be depolymerized, and the monomers degraded to lower molecular weight products (1, 14, 17–23).

Occasionally the literature has reported the electrochemical reduction of aldoses (16, 24) and other carbohydrates (25), and of aliphatic and aromatic aldehydes (26–28). The mechanism of such a reduction of glucose, which produced as side-products small amounts of mannitol and 2-deoxyglucitol, was elucidated by Wolfrom *et al.* (29, 30).

The qualitative and quantitative study reported herein was instigated to determine the effect on simple carbohydrates of electrolysis in a system in which the generation of a significant concentration of methoxyl free radicals could be anticipated (31).

Discussion

Paper chromatographic analysis of the products of electrolysis revealed the stepwise degradation of the parent compound to a mixture of lower aldoses (Table I). In accord with earlier studies (14), these reactions exhibited a high initial rate. In one typical experiment, a detectable amount of the secondary reaction, arabinose → erythrose, was obtained after 10 min electrolysis of D-glucose. D-Galactose underwent a more efficient degradation than D-glucose and gave a higher yield of pentose (cf. ref. 20).

A large volume of gas containing both H_2 and CO_2 was evolved during the reaction, principally from the cathode. Whereas it is likely that the H_2, and much of the CO_2, came from the electrolysis of methanol (31), the lack of quantitative recovery of carbohydrate suggested that some of the parent compound was completely oxidized to CO_2 (18).

Experiments in which maltose, because of its low solubility in methanol, was electrolyzed in water to which sodium methoxide was added, disclosed rapid and extensive cleavage of the glycosidic bond. Paper chromatographic analysis revealed no identifiable oxidation product of maltose; glucose and arabinose were the earliest degradation products detected (see Table I). These observations are consistent with an initial

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[3]To whom enquiries should be addressed.

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[5]Deceased.

TABLE I

Results obtained from the electrolysis of various carbohydrates under a variety of conditions

Experiment number	Compound (amount used in g)	Solvent (amount used in ml)	Electrolyte (amount used in mg)	Current (max. V, max. A, type*)	Time (h)	Chromatographic analysis	
						Products†	Solvents
1	D-Glucose (10)	EtOH (200)	Na (80)	—,—,*d*	7	G;Ara;Ery	*a,b,c*
2	D-Glucose (10)	MeOH (200)	KOH (80)	—,—,*d*	24	G;Ara;Ery	*a,b,c*
3	D-Glucose (15)	MeOH (200)	Na (50)	40,—,*a*	21	G;Ara;Ery	*a,b,c*
4	D-Glucose (10)	MeOH (230)	Na (30) V_2O_5 (1)	40, 0.3,*d*	22	G;Ara;Ery	*a,c*
5	D-Glucono-1,5-lactone (10.5)	MeOH (200)	Na (55)	40,—,*a*	24	GA;Ara;Ery	*b,c*
6	Methyl-α-D-glucopyranoside (2)	MeOH (200)	Na (40)	50, 0.3,*d*	36	Unk;G;MeG	*f*
7	D-Galactose (9)	MeOH (200)	NaOH (70)	46, 0.7,*d*	21	Gal;Lyx;Thr‡	*b,c,d*
8	D-Galacturonic acid (5)	MeOH (200)	Na (50)	60,—,*a*	44	Gal A;Ara	*d*
9	D-Mannose (3)	MeOH (100)	Na (30)	47, 0.2,*d*	24	Man;Ara;Ery	*a,c,d*
10	Maltose (10)	H_2O (250)	Na (60) in MeOH (3 ml)	47, 0.45,*d*	24	Mal;G;Ara;Ery	*b,c*

d, direct current; *a*, alternating (60 Hz) current.

†The abbreviations used are: Ara, arabinose; Ery, erythrose; Gal, galactose; Gal A, galacturonic acid; G, glucose; GA, gluconic acid; Lyx, lyxose; Mal, maltose; Man, mannose; MeG, methyl glucoside; Thr, threose; Unk, unidentified. Products are listed in order of increasing R_f.

‡Identified as threitol after reduction with $NaBH_4$.

hydrolysis of the glycosidic bond followed by the usual electrolytic degradation of glucose, and with the synthesis of 3-*O*-α-D-glucopyranosyl-D-arabinose (32) followed instantly by hydrolysis to D-glucose and D-arabinose. The elucidation of the route(s) is under investigation.

As adduced from qualitative paper chromatographic analysis, the same products were obtained by electrolysis with each of sodium methoxide, sodium ethoxide, sodium hydroxide, and potassium hydroxide (see Table I).

In this study an amperage lag of 0.1–0.5 min occurred at the start of electrolysis before the amperage rose to a maximum value (usually after 0.1–0.5 h) and thereafter slowly declined. The porosity of the graphite electrodes and/or the formation of an insulating residue on the cathode surface may explain in part this decline. However, the reversal of polarity, which caused the residue to flake off of the new anode, and/or the cleaning of the electrode surface, failed to restore maximum current. Some current-conducting component appeared to have been consumed or otherwise irreversibly removed from the system.

The non-aqueous system was peculiar in that it formed aldoses in the absence of chromatographically detectable quantities of aldonic acids (3–9, 14, 16) and other oxidized derivatives (4, 14, 15). Nevertheless the most probable mechanism of sequential degradation would involve the formation of an aldonic acid as the first, or an early, step in the electrolysis, since these are known to form from (16, 17), and to degrade to (14, 20, 33), aldoses during electrolysis. Neuberg's (14) discovery of ozones in the electrolysis of aldoses may mean that an α-keto compound is formed (34) either prior to, or after, the carboxyl group, thus giving an α-ketoaldonic acid which can decarboxylate to an aldose having one less carbon atom (35). Consistent with such a theory are the alkaline oxidative degradation of D-glucose to D-arabonic acid (36) and L-arabinose to L-erythronic acid (37), the formation in alkali of carbonyl derivatives of carboxylic acids (31), and the detection of a keto acid from the electrolysis of erythronic acid (21). If such acidic intermediates participate in these reactions the aldoses must be strongly favored in any equilibria involving the oxidized compounds, and/or the oxidation must be very slow relative to decarboxylation so that at any instant the concentration of the intermediate is below present levels of detection.

Electrolysis offers a facile, and potentially useful method for the sequential degradation of sugars, and sugar derivatives (14, 33) to lower homologues. The method is of broad application (Table I, see ref. 33) and avoids the necessity of synthesizing special derivatives (38) for subsequent chemical degradation. Both the mechanism of the process, and conditions whereby higher yields of a desired product can be obtained, remain to be established, however, even in its present state of development it is a practical means of obtaining certain unusual sugars such as D-arabinose and D-threose in semi-micro amounts, as has been clearly established by the isolation of milligram quantities of the pure products by preparative paper partition chromatography. There seems to be no reason to question the ability of still more recent separatory techniques to provide equal or superior resolution and recovery of the individual components on a macro scale.

Experimental

General Methods

All evaporations were carried out at 35–45 °C under reduced pressure, unless stated otherwise. Melting points were determined with a Fisher–Johns Melting Point Block (Fisher Scientific Co.) and are uncorrected. The water used for optical rotation studies of free sugars contained a trace of ammonium hydroxide to catalyze the formation of an equilibrium mixture of anomers.

Paper chromatography by the descending technique, using Whatman no. 1 and 3MM paper, was effected with one or more of the following solvent systems (39): (*a*) 1-butanol:ethanol:water, 4:1:5; (*b*) 1-butanol:pyridine:water, 6:4:3; (*c*) pyridine:ethyl acetate:water, 2:5:7; (*d*) 1-butanol:acetic acid:water, 2:1:1; (*e*) 2-butanone–water azeotrope; (*f*) ethyl acetate:acetic acid:formic acid:water, 18:3:1:4. Chromatograms were visualized (39) with ammoniacal silver nitrate, or with *p*-anisidine–trichloroacetate.

Electrolysis Cell and Power Supplies

The cell was a standard 800 ml (13 × 9.5 cm) beaker which was slightly reshaped to remove the pouring lip. Two holes were drilled in a stopper (size 15) to accommodate 4.0 cm diameter graphite electrodes approximately 0.5 cm apart. Each electrode was fitted with a brass terminal at the exterior end. A third hole was drilled in the stopper in which was inserted a 19/38 to 24/40 standard taper adapter which received a reflux condensor.

A power supply from a Reco Electric Desalter (Research Equipment Corp.) with a maximum output of 3.0 A at 50 V, or a transistorized rectifier module (fused at 2 A) attached to a Powerstat variable resistance (The Superior Electric Co.), supplied direct current for the experiments. The Powerstat control without rectifier was used to supply alternating current (60 Hz).

General Electrolytic Method

In almost all experiments, the sugar sample and the solvent were introduced into the dry, sealed electrolysis cell. The electrodes extended 3.5–4.5 cm below the surface of the reaction mixture. The electrolyte (Na, NaOH, KOH, or $NaOCH_3$) was dissolved whereupon the voltage was applied to give maximum current. Electrolysis was continued for widely variable lengths of time.

Miscellaneous Electrolyses

A relatively large number of experiments were investigated only by qualitative paper partition chromatographic analysis. The results of a series of typical experiments are recorded in Table I.

Electrolysis of D-*Glucose*

A sample (15.0 g) of D-glucose (anhydrous powder) was suspended in 200 ml methanol to which 0.05 g freshly cut sodium then was added. The solution was electrolyzed for 44 h using direct current (d.c.). The current rose to a maximum of 1.1 A at 45 V after 0.5 h and then declined slowly to a terminal value of 0.15 A at 47 V. Aliquots were removed 3, 5, 15, 24, and 44 h after the start of the experiment and were found by paper partition chromatography in solvents *a*, *b*, and *c* to contain glucose, arabinose, erythrose, and some unidentified material. Evaporation of the solvent gave 8.2 g of heavy, amber syrup.

A sample (0.3587 g) was resolved quantitatively by preparative paper chromatography in solvents *a* and *b*. The components having R_f values greater than that of erythrose were reduced with sodium borohydride whereupon glycerol was detected. The individual components were isolated and identified in the following manner.

D-Glucose: glucose (0.2208 g, yield: 51.0%) $[\alpha]_D^{24}$ +54.0° (*c*, 1 in H_2O) (40), was converted to the characteristic *N*-*p*-nitrophenyl-β-D-glucosylamine, m.p., and mixture m.p. 184.5–186 °C (41).

D-Arabinose: this component (0.0528 g, yield: 12.4%) $[\alpha]_D^{25}$ −101° (*c*, 0.8 in H_2O) (42), afforded D-arabinose benzoylhydrazone, m.p. and mixture m.p. 189–190 °C (hot, 95% ethanol) (43).

D-Erythrose: this fraction (0.0430 g, yield: 9.9%) $[\alpha]_D^{24}$ −15.5° (*c*, 1 in H_2O) (44–46), was reduced in aqueous solution $NaBH_4$. Erythritol was characterized as the tetra-*p*-nitrobenzoate, m.p., and mixture m.p. 249–251 °C. An authentic sample had the same m.p.

Glyceraldehyde: the components migrating faster than erythrose on the paper chromatograms were eluted with water, reduced with $NaBH_4$, and rechromatographed after removal of borate (47). Glycerol (0.0181 g, yield: 4.2%) was identified as the tri-*p*-nitrobenzoate, m.p., and mixture m.p. 191–192.5 °C (48).

The remaining eluates were combined and evaporated to a light-amber syrup (0.0161 g, yield: 3.7%).

Control Experiment

A duplicate solution of D-glucose in sodium methoxide–methanol was refluxed for the period during which electric current was allowed to flow.

Chromatographic analysis of the reaction product in solvents *a* and *d*, revealed the presence of glucose with traces of mannose and arabinose.

Electrolysis of D-*Galactose*

D-Galactose (9.1 g) was electrolyzed in 200 ml methanol to which was added 0.04 g sodium. A direct current was passed through the solution for 20 h using graphite electrodes. The current rose to a maximum of 0.9 A at 44 V after 0.25 h and thereafter declined to the terminal value of 0.55 A at 46 V. Evaporation of the reaction mixture gave 8.6 g of viscous syrup.

A sample (0.1631 g) was resolved by paper chromatography in the manner described for glucose, except that the components migrating ahead of lyxose were eluted, combined, reduced, and rechromatographed. The individual components were identified on the basis of the following data:

D-Galactose: galactose (0.0466 g, yield: 27.0%), $[\alpha]_D^{25.5}$ +78.4° (*c*, 1.2 in H_2O) (40), was converted in the usual manner to D-galactose *unsym*.-methylphenylhydrazone, m.p. and mixture m.p. 186–187 °C (43).

D-Lyxose: this component (0.0413 g, yield: 24.0%) $[\alpha]_D^{24.2}$ −12.6° (*c*, 1 in H_2O) (42), afforded the 2,5-dichlorophenylhydrazone of D-lyxose, m.p. and mixture m.p. 140–142.5 °C (hot aqueous ethanol) (49).

D-Threitol: threitol (0.0293 g, yield: 17.0%) $[\alpha]_D^{25.2}$ +4.5° (*c*, 4.75 in H_2O) (50–51), was converted in the usual manner to di-*O*-benzylidene-D-threitol, m.p. 222–223.5 °C, mixture m.p. 224–225 °C (52).

Glycerol: this component (0.0094 g, yield: 5.4%) was identified as described above (48).

The unidentified residue weighed 0.0329 g, yield: 19.1%. A control experiment was performed in the usual manner.

Analysis of Electrode Gases

The electrolysis of 10 g D-glucose in 200 ml methanol in which 0.05 g sodium had been dissolved, was allowed to proceed for 6 h to displace air initially present in the cell. The evolved gas was passed into a clear solution of $Ba(OH)_2$. The formation of a white precipitate was accepted as a presumptive test for CO_2.

A similar experiment was performed on a smaller scale using an "H" tube to separate the anode and cathode. Cathodic gases were collected under water. The water vapor was frozen out with Dry Ice – acetone and the gases analyzed in a mass spectrometer.[6] Hydrogen was identified as a major component of the mixture.

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[6]The mass spectrometric analyses were obtained through the courtesy of Dr. J. A. Stone, Department of Chemistry, Queen's University.

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