JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) · TECHNICAL NOTE

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Electrolytic preparation of 2-osuloses: a route to *L*-ascorbic acid

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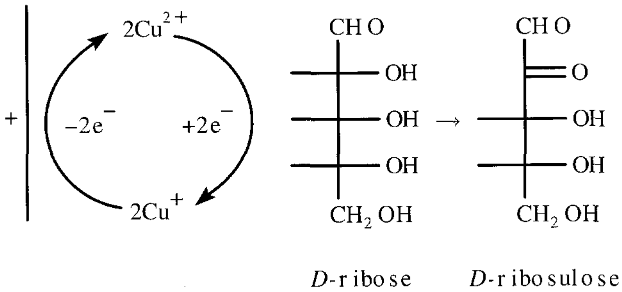
Received 18 October 1992; revised 1 February 1993

1. Introduction

The chemical oxidation of aldopentoses and ketohexoses by copper (II) acetate in water/methanol as solvent is a well known procedure for the synthesis of 2-osuloses [1,2]. This reaction is a step in one of the pathways to *L*-ascorbic acid [3] and related compounds [4]. However, a large excess of copper (II) is needed to carry out the reaction, which is cumbersome from an environmental standpoint. Therefore, a procedure which overcomes this problem is of potential industrial interest. Indirect electrosynthesis has been shown to be a useful tool for avoiding this kind of problem [5–8].

In this note, a preliminary study at laboratory scale, to test the possibility of obtaining 2-osuloses by indirect electrooxidation of aldophentoses and ketohexoses, using an in-cell method, is reported. As an example of the proposed method, Scheme 1 depicts the indirect electrooxidation of *D*-ribose to *D*-ribosone.



Scheme 1

2. Experimental details

2.1. Synthetic procedures

A stirred solution of the aldopentose or ketohexose (0.02 mol), sodium acetate (0.02 mol) and copper (II) acetate (0.25×10^{-2} mol) in 50 cm^3 of methanol : acetic acid : water (12 : 1 : 2), was contained in the anodic part of a cell with a porous glass diaphragm; 20 cm^3 of a solution of sodium acetate (0.02 mol) in the same solvent mixture was used as catholyte. Current was supplied from an Arrosu rectifier (5 A, 100 V). Platinum was used as anode, and copper, platinum and carbon as cathodes. The preparative electrolyses were carried out at constant current (2 A; current density was 0.1 A cm^{-2}) and were stopped after a charge of 6 F mol^{-1} was passed. Depending on the interelectrode gap, the cell voltage ranged between 25 and 30 V. The electrolyses were carried out at reflux temperature and, at the end of a run, the solution was filtered through Amberlite® IR-120 (cation exchange resin) and Amberlite® IRA-400 (anion exchange resin). The resins were previously converted to their H^+ and OH^- forms, respectively. The filtrate was concentrated and dried by evaporation at 30–40° C under reduced pressure.

2.2. Analysis

Identification of the products of the electrochemical reaction was made by paper chromatography, and by both GLC and GLC-MS of their trimethylsilyl and isopropylidene derivatives.

Descending paper chromatography was performed on Whatman No. 1 paper with 1-butanol-acetone-water (7 : 2 : 1). Detection was effected with aniline hydrogen phthalate in 1-butanol, $AgNO_3$ in acetone and basic solution, and by orcinol–Cl_3C–COOH. Trimethylsilylation of the dry syrupy products was performed by the usual method [9]. Isopropylidenation was performed as in a previous paper [10]. GLC measurements were carried out by means of a Perkin–Elmer chromatograph model 3920 B with a column (4 m × 0.32 cm) packed with SE-52 on Chromosorb W (80–100 mesh). The initial temperature was 80° C. The column temperature was increased at 2° C min^{-1} from 80 to 250° C. The analysis time at 250° C was 30 min. Mass spectra (70 eV) were obtained with a Hewlett–Packard gas chromatograph model 5710 A coupled to a mass spectrometer model 5980 A. The yields were calculated from the

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GLC chromatograms with *D*-arabinose as internal standard.

3. Results and discussion

The indirect electrooxidation of *D*-xylose, *D*-arabinose, *D*-ribose, *D*-fructose and *L*-sorbose under the reaction conditions described above leads to the corresponding 2-osuloses with a conversion of 100% and material yields ranging from 48 to 55%, identical to those obtained in a parallel assay for the chemical reaction with a large excess (3–4-fold) of copper (II) acetate in methanol at reflux temperature. However, the amount of chemical oxidant involved in the electrolytic reaction is at least 20-fold lower than that in the chemical reaction. In addition, there is practically no consumption of copper (II) during the electrolysis. In some experiments, in which platinum and carbon were used as cathodes, a slight coloration of the cathode surface indicated copper electrodeposition, but the amount was low.

These preliminary results show that the electrolytic procedure works with a small amount of copper (II) acetate, which is electroregenerated during the electrolysis, and that the copper (II) involved in the reaction can be reused. However, the experimental conditions tested in the few experiments carried out so far, are still far from the industrial requirements. Nevertheless, taking into account the drastic experimental conditions used, further improvement of the yield may be expected by careful choice of the charge (which in this study was passed in large excess), temperature, electrolyte and electrodes. The use of an undivided flow cell would permit a large reduction in the interelectrode gap and, consequently, the cell voltage and power consumption. Similarly, this kind of cell, with both electrodes of the same material (platinum or carbon), would allow the polarity of the electrodes to be reversed from time to time to avoid copper electrodeposition on the cathode surface.

4. Conclusions

Indirect electrosynthesis of 2-osuloses from aldopentoses and ketohexoses has shown to be an interesting tool for reducing the amount of chemical oxidant (copper (II)) involved in the reaction. However, the experimental conditions under which the reaction is carried out are far from those industrially acceptable. Nevertheless, the potential advantages of the electrolytic method, as well as its interest in organic synthesis, are so important that further effort should be spent in studying this procedure.

Acknowledgements

One of the authors (F.B.) is indebted to the Comunidad de Madrid for financial support (Grant C018/90).

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