JOURNAL OF APPLIED ELECTROCHEMISTRY 27 (1997) 25–33

Electrocatalytic oxidation of sucrose: analysis of the reaction products

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Received 21 January 1996; revised 21 March 1996

The analysis of sucronic acids produced by the electrocatalytic oxidation of sucrose is described. The main reaction products, 1′-monocarboxylic and 6-monocarboxylic acids of sucrose, were identified by means of gas and liquid chromatography, mass spectrometry, NMR and i.r. spectroscopy, and acid hydrolysis. The quantitative analysis of reaction products other than the sucronic acids was realized by ionic chromatography (Dionex), whereas that of the sucronic acids was carried out using their acid hydrolysis products.

1. Introduction

The detailed analysis of the reaction products involved in the chemical transformation of sucrose faces problems connected with the analytical procedures. As a first attempt in applying electrocatalysis to make use of carbohydrates, the regioselective electrocatalytic oxidation of sucrose, glucose or gluconic acid was investigated. Corresponding acids or ketones were selectively produced [1–4]. The importance of this topic lies in the possible use of these oxidation derivatives in pharmaceutical and agricultural chemistry.

Monocarboxylic acids of sucrose are important intermediates in the selective synthesis of monoesters and monoamides of sucrose (tensioactive compounds). In particular, the uronic and 2-keto aldonic acids obtained by hydrolysis of the monocarboxylic acids of sucrose are of industrial interest in the fields of environmentally friendly detergents, emulsifiers and pharmaceuticals.

Only a few papers have mentioned the monocarboxylic acids of sucrose. Court describes the electrocatalytic oxidation of sucrose at nickel electrodes [5]. Preliminary investigations of the reaction products by spectroscopic, analytical and chemical derivatization techniques led the author to conclude that the oxidation of the primary hydroxyl groups was selective. However, in spite of some attempts, the analytical techniques available at that time did not allow the complete identification of all the reaction products.

More recently, among the products of the catalytic oxidation of sucrose on platinum at neutral pH, Edye *et al.* [6] isolated the ammonium salts of 6′-monocarboxylic and 6,6′-dicarboxylic acids. They identified the above products by NMR spectroscopy and by chromatography of the invertase hydrolysis products.

The present work aims to describe the analytical procedures developed for the identification of the sucronic acids synthesized from the electrocatalytic oxidation of sucrose in alkaline medium on platinum modified by underpotential deposition of lead adatoms (upd-Pb).

2. Experimental details

2.1. *Electrolyses*

Programmed potential electrolysis was the main electrochemical method used in this work [7]. It consists in controlling the oxidation potential which, by itself, is a parameter of selectivity. Because of the poisoning phenomena occurring in long-term electrolysis and in order to maintain the electrode activity at a sufficient level, the electrolyses were carried out using an optimized programme of potential which included three potential plateaus. The electrolysis oxidation plateau was applied for 14.8 s in a potential range corresponding to the maximum of electrode activity (0.73 V vs RHE). Then the electrode surface was reactivated by clearing out the poisoning species by oxidation at 1.63 V vs RHE during 0.2 s. The third pulse was set at around 0.23 V vs V RHE for 1 s allowing the reduction of the surface and/or the *in situ* underpotential deposition of adatoms. This sequential unit programme was repeated during throughout the electrolysis (Fig. 1).

The electrolyses were carried out in deaerated aqueous solutions, prepared with 'ultrapure' water (18 MΩ cm, Millipore Milli Q system). Aqueous

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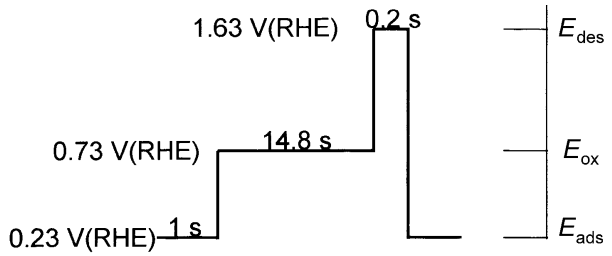


Fig. 1. Potential programme used for long term electrolysis of sucrose.

solutions of 'suprapur' $NaHCO_3$ and Na_2CO_3 (purchased from Merck) were used as electrolytes. The sucrose (99%) was supplied by Fluka. Electrolyses were performed in a filter press cell (microflow cell, Electrocell AB) (Fig. 2). The working electrode was platinum deposited electrochemically at a titanium plate. The counter electrode was a plate of stainless steel (2343). The two-compartments of the cell were separated by an ion-exchange membrane (Nafion 423®). To control the electrode potential, a part of this membrane and the reference electrode (MSE) were connected together by immersing them in a saturated solution of K_2SO_4. However all potentials are referred to the reversible hydrogen electrode (RHE). The electrolyte in the cell was circulated by an external peristaltic pump (1 cm^3 min^{-1}) and passed through a reservoir (100 cm^3).

The electrochemical instrumentation consisted of a Hewlett Packard HP 33120A Arbitrary Waveform Generator coupled to a Bank High Power Potentiostat (Wenking Model HP88). The potential programme was synthesized using a HP BenchLink software (HP BenchLink/Arb) under a Windows™ environment; it was then transferred to the function generator. Data such as applied potential, current intensity and quantity of electricity were acquired by a PC 486/33 MHz microcomputer equipped with an AD/DA converter (Keithley DAS 20-Viewdac).

2.2. *Analytical equipment and analytical procedures*

Quantitative analysis of the reaction products was performed by high performance ionic chromatography (HPIC) using an ion-exchange liquid chromatograph (Dionex 4500i). This worked with a ternary gradient of elution. The partition was carried out on high performance anionic column (AG11+AS11, Dionex). A double detection system (a conductimeter and a refractometer, both online) allowed to monitor the ionizable and nonionizable molecules. High performance liquid chromatography (HPLC) was carried out using an isocratic pump (Knauer) and a double detection system including an ultraviolet detector and a refractometer. The product partition was carried out on an ion exchange column (Aminex HPX-87H, Biorad). Gas chromatography (GC) was performed with a Varian gas chromatograph using a DB-5 capillary column (95% dimethyl-5% diphenyl-polysiloxane bonded, 30 m, 0.25 mm i.d. and 0.25 μm film thickness). This was combined with a mass spectrometer (INCOS 500).

Proton decoupled and ^{13}C, pulse Fourier transform NMR spectra were recorded with a Brucker WP 200SY spectrometer (200 MHz), using CD_3OD solutions of tetramethylsilan or aqueous solutions (D_2O) of

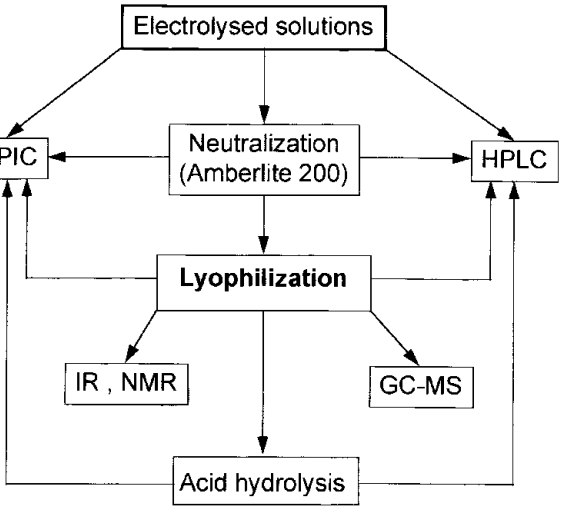


Fig. 3. Analytical procedure used for the full determination of the sucrose oxidation products during and after long-term electrolyses.

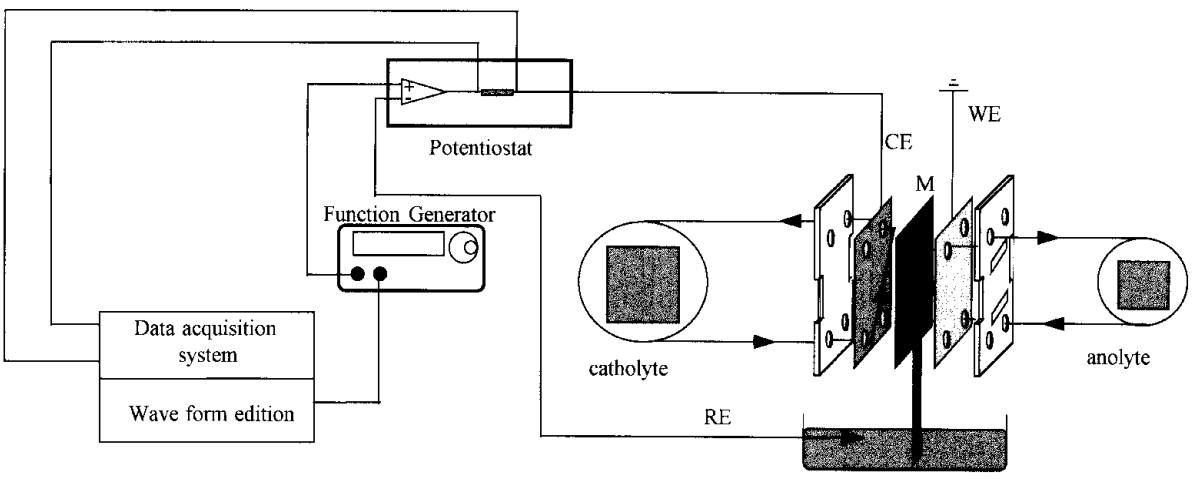
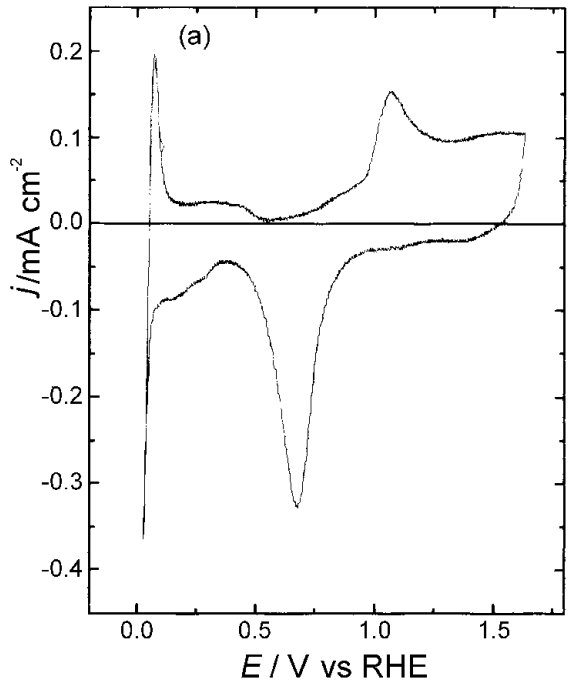


Fig. 2. Experimental setup used for prolonged electrolysis of sucrose. Key: CE= counter electrode; RE= reference electrode; WE= working electrode; M = ion exchange membrane.



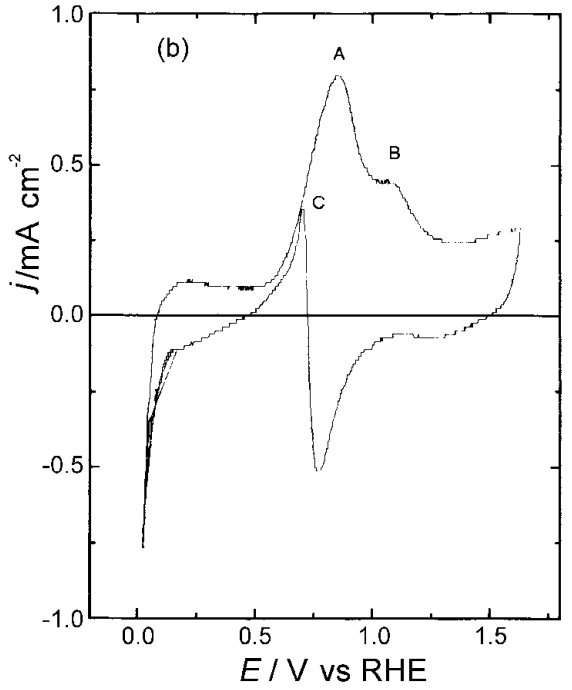


Fig. 4. Voltammograms of platinum recorded at 50 mv s^{-1} and at room temperature: (a) supporting electrolyte 0.1M Na_2CO_3–$NaHCO_3$ in the presence of lead adatoms (10^{-5} M Pb^{2+}) and (b) in the presence of 10.2 mM sucrose.

methanol, as internal references. Infrared spectra were obtained using a Nicolet analytical system (10 MX).

The electrolysed solution was hydrolysed in 1M $HClO_4$. The solution was then analysed by liquid chromatographies (HPLC and HPIC).

The flow chart represented in Fig. 3 summarizes the different experimental steps applied to the reaction mixtures during their qualitative and quantitative analyses.

3. Results and discussion

3.1 *Electrochemical results*

Before each electrolysis, a voltammogram was recorded in order to establish the potential programme. Figure 4 shows the voltammograms of a lead modified platinum electrode, in 0.1M Na_2CO_3–$NaHCO_3$, in the absence (a) and presence of 10.2 mM of sucrose (b). These were recorded at 50 mV s^{-1}, at room temperature and in the presence of 10^{-5} M Pb^{2+}. During the positive variation of potential, two oxidation peaks of sucrose, A and B, are observed at 0.8 V vs RHE ($j = 0.8$ mA cm^{-2}) and at 1.1 V vs RHE ($j = 0.44$ mA cm^{-2}). During the negative variation of potential, another peak, C, is noticed at 0.7 V vs RHE ($j = 0.3$ mA cm^{-2}) after the desorption of the oxygenated species from the electrode surface.

Electrolysis of sucrose was carried out under the same experimental conditions for 8.3 h with the potential programme described in Fig. 1. The quantity of electricity at each potential plateau was evaluated and presented in Fig. 5. It is seen that Q_{des} and Q_{ads} have an almost symmetrical profile with a small advantage for Q_{ads}.

Q_{ads} is the quantity of electricity which served to adsorb the organic molecule and eventually to reduce the electrode surface. It may be assumed that Q_{des} was used for removing the poisoning organic species from the electrode surface. But, if the active surface of platinum was covered by OH_{ads} at the desorption plateau (1.63 V vs RHE), after 8.3 h of electrolysis, $Q_{(OH)ads}$ would be estimated as follows:

$$Q_{(OH)ads} = n \times e^- \times (OH)_{ads} \times S_a \times \tau \qquad (1)$$

where n is the electron number ($n = 1$), e^- is the electron charge, $(OH)_{ads}$, the number of adsorbed hydroxyls (i.e., the number of platinum sites (1.3×10^{15})); S_a is the active surface area of the working electrode (45 cm^2) and τ is the number of cycles with t_{des} (0.2 s) used during the electrolysis ($\tau = 1852$), which gives $Q_{(OH)ads} = 17.34$ C.

This estimation is close to the experimental value ($Q_{des} = 19.7$ C). This means that the electrooxidation of sucrose was realized at 0.7 V vs RHE with nearly no poisoning species involved. Thus, the quantity of electricity for sucrose oxidation was Q_{ox} and, at the end of electrolysis, this value was estimated as 104 C.

During prolonged electrolyses, samples from the electrolysed solution were analysed by ionic chromatography. The quantitative analysis of sucrose monitored by the differential refractive index detector gives the conversion yield and information on the reaction products. The chromatographic analysis reveals small amounts of several well-known reaction products (formic, glyceric, tartaric, mesoxalic, glucuronic, oxalic and glycolic acids) and two important peaks, noted A and B (Fig. 6), corresponding to the main products of electrooxidation of sucrose.

At the end of the electrolysis, the yield of the sucrose transformation was estimated as close to 60%. The solution was sampled and neutralized on

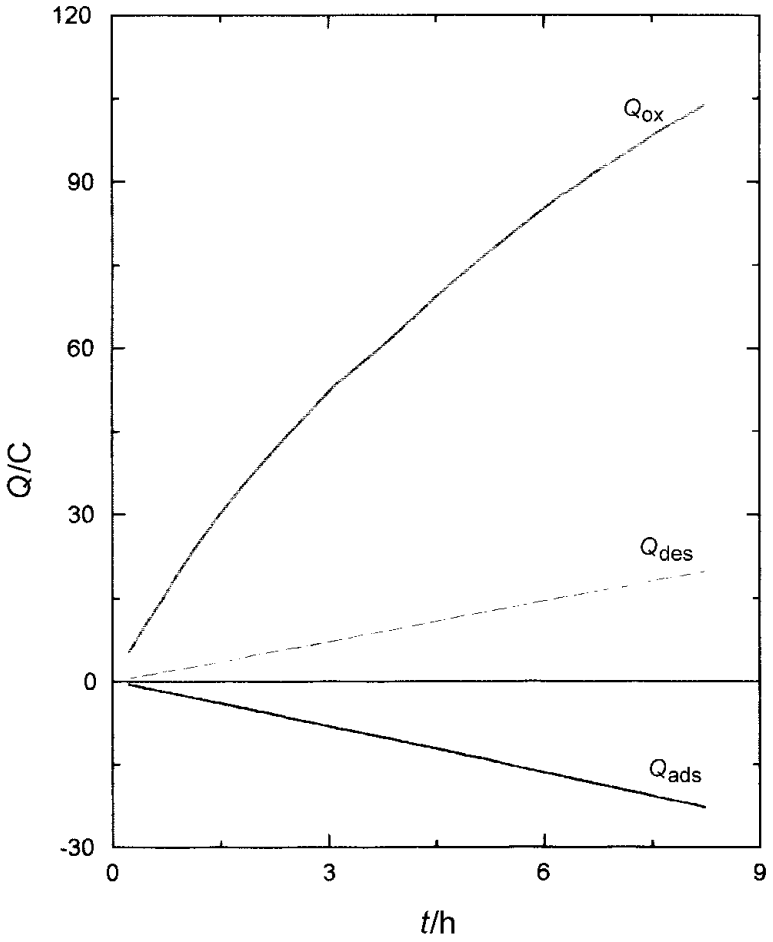


Fig. 5. Variation of the quantities of electricity against the time of electrolysis.

a cation exchange resin (Amberlite 200, Sigma). The solutions obtained, free from inorganic cations (Na^+), were chromatographed again to be sure of the reproducibility of the last analysis. The final pH was 2.8. Then, water was removed by lyophilization to dry the reaction products. Samples from the lyophilized material were then taken for infrared, NMR, acid hydrolyses and CG-MS analyses.

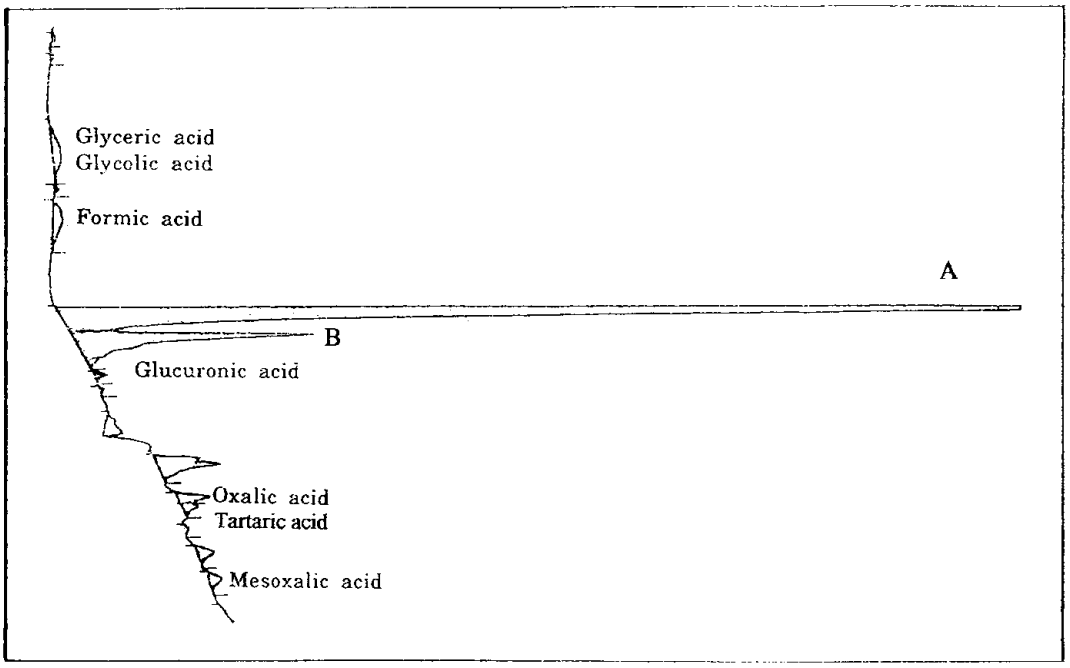


Fig. 6. Chromatogram recorded at the end of the sucrose electrolysis on an upd-lead modified platinum electrode.

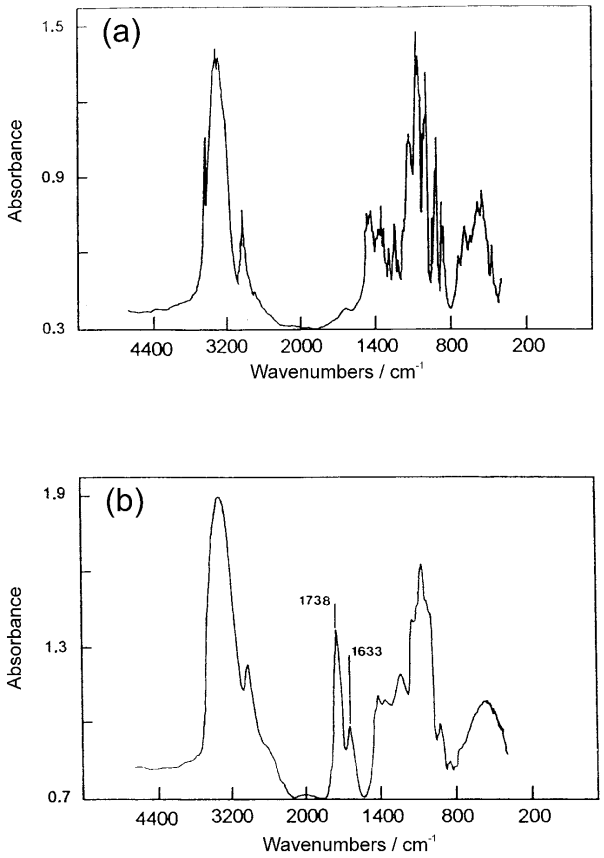


Fig. 7. KBr pellet infrared spectra of (a) pure sucrose and (b) lyophilized electrolysis products of sucrose on an upd-lead modified platinum electrode.

3.2. *Infrared spectroscopy*

For recording the infrared spectra, the lyophilized reaction products were dispersed in KBr pellets. Infrared spectra of sucrose and lyophilized oxidation derivatives of sucrose are represented in Fig. 7(a) and (b), respectively. The infrared spectrum of the dried electrolysis products shows two intense bands ($1738\,cm^{-1}$ and $1633\,cm^{-1}$), which are not seen in the infrared spectrum of the starting material. Except for these two bands, the spectrum is not significantly different from that of pure sucrose. This indicates that the ring structure of the carbohydrate is not substantially changed during electrolysis. Moreover, the structure of the products must have a strong relationship with the structure of the starting material. The band at $1738\,cm^{-1}$ corresponds to the vibration of a free acid [8]. The absorption band at $1633\,cm^{-1}$ is assigned to traces of water which can be explained by the hygroscopic nature of the lyophilized material.

3.3. *Acid hydrolysis*

The acid hydrolysis rate was followed by HPLC (HPX-87H Aminex column) and HPIC (AG11+AS11 Dionex column). HPIC analyses of the lyophilized reaction products before and after hydrolysis allowed separation of peak A from its ionizable hydrolysis product i.e. 2-keto-gluconic acid, as identified by conductimetric detection. The non-ionizable hydrolysis product was glucose as identified by refractometric detection. At the end of hydrolysis, peak A disappeared completely. The weight ratio of 2-keto-gluconic acid to glucose led to the conclusion that peak A (see Fig. 6) corresponds to the 1′-monocarboxylic acid of sucrose (1′-MAS). See Scheme 1.

In the same way, with an adapted elution gradient, peak B (see Fig. 6) was found to correspond to the 6-monocarboxylic acid of sucrose (6-MAS), which by acid hydrolysis, led to glucuronic acid and to fructose. See Scheme 2.

3.4. *Mass spectrometry*

The lyophilized material was prepared for GC-MS measurements by trimethylsilylation according to the procedure developed by Sweeley *et al.* [9], using hexamethyldisilasane and trimethylchlorosilane as silylation reagents.

Figure 8 represents the chromatograms of the

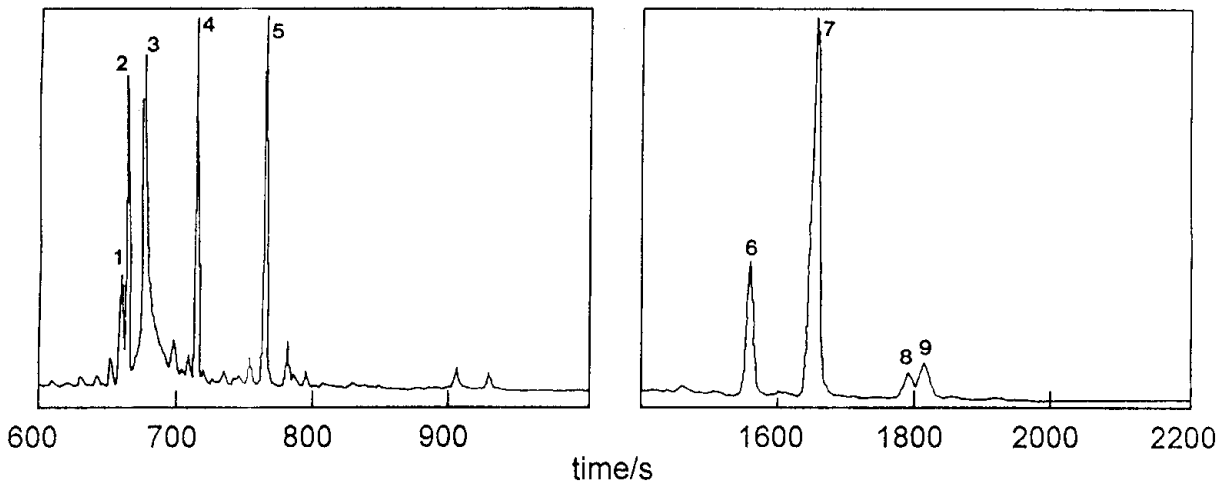
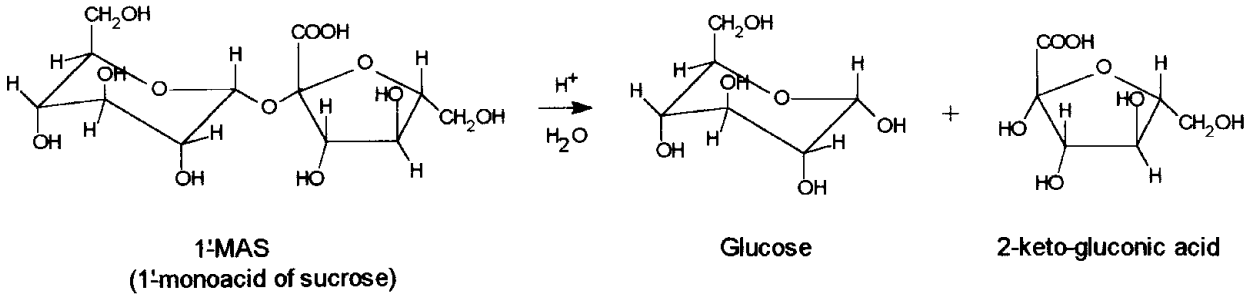
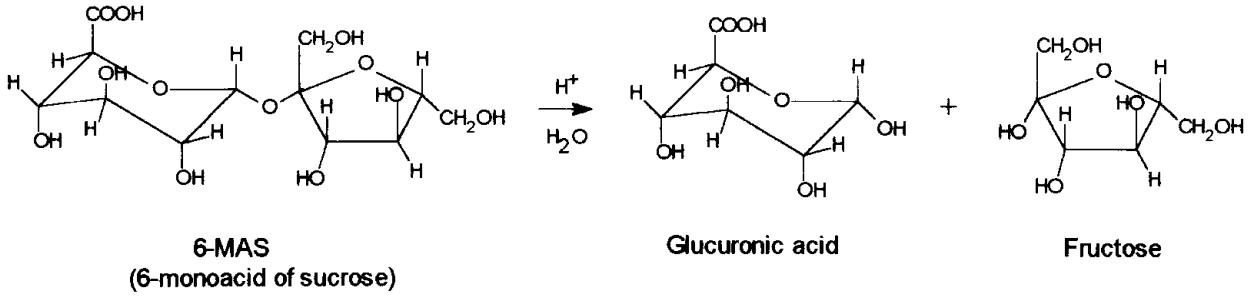


Fig. 8. Gas chromatography analysis of the trimethylsilylated products of the electrocatalytic oxidation of sucrose on an upd-lead modified platinum electrode.



Scheme 1



Scheme 2.

trimethylsilylated products resulting from the electrocatalytic oxidation of sucrose. The peaks quoted 1, 2, 3 and 4, 5 correspond to the different anomeric and cyclic forms of the TMS derivatives of fructose and glucose, respectively. These peaks were identified by comparison with the mass spectra of TMS derivatives prepared from authentic glucose and fructose. In the same way, the peak quoted 6 was identified as the TMS derivative of sucrose.

From the data compared in Table 1, it is clearly seen that peaks 6, 7, 8 and 9 led practically to the same fragmentation paths. A preferential cleavage of the glycosidic bond places the charge on the carbon next to a ring oxygen where it can be stabilized by the non binding electrons of oxygen [10]. The only exception is the ions at $m/z = 375$ and 465 observed in the case of the three peaks 7, 8 and 9.

Molecular ions were not observed in the mass spectra because of the absence of metastable ions in the range of the higher masses.

In the case of sucrose, two stabilized fragments may arise from the breaking of the glycosidic bond depending on moieties, glucose or fructose, which retain the oxygen atom. See Scheme 3.

Consequently, in all cases, the relative intensities of $m/z = 361$ result from the statistical loss of HO-TMS [11]. See Schemes 4 and 5.

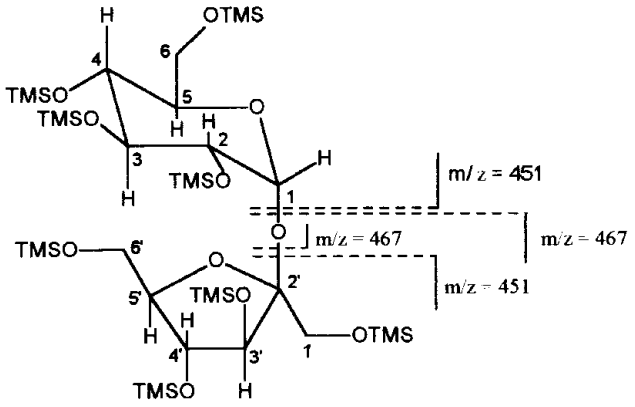
The series of low-intensity peaks at $m/z = 421, 436,$

Table 1. Abundance (%) of the main fragments from the mass spectra of sucrose and peaks quoted 7, 8 and 9 in Fig. 8

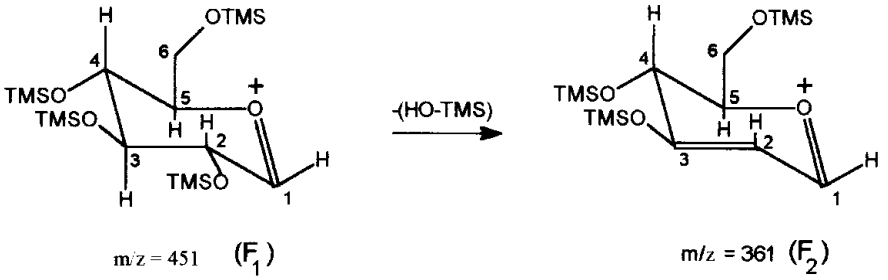
m/z	*Sucrose (peak 6)*	*Peak 7*	*Peak 8, 9*	*Fragments*
73	100	100	100	$(TMS)^+$
103	36.8	16.9	12.2	$(CH_2=OTMS)^+$
147	31.2	28.7	20.6	$(CH_3)_3SiOSi(CH_3)_3$
217	47.2	23.4	23.7	H_2(TMSO)C–C=C(OTMS)H
361	52.8	17.2	13.7	F_2 or F'_2 (see text)
375	—	34.1	13.1	F_4 or F'_4 (see text)
421	0.1	0.2	0.1	F_1-30 or F'_1-30
436	0.1	0.1	0.1	F_1-15 or F'_1-15
437	3.0	0.1	2.0	467–30
451	1.0	1.8	0.3	F_1 or F'_1 (see text)
452	0.4	0.3	0.2	467–15
465	–	0.2	1.1	F_3 or F'_3 (see text)

Table 2. Chemical shifts of the ^{13}C NMR spectrum of the lyophilized reaction products obtained on an upd-Pb/Pt electrode in comparison with those of pure sucrose

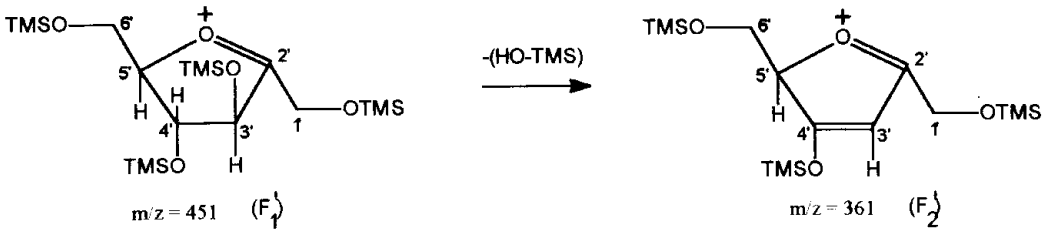
Carbon number	C1	C2	C3	C4	C5	C6	C′1	C′2	C′3	C′4	C′5	C′6
Sucrose	93	72	74	70	73	61	63	104	77	75	82	63
Reaction products	94	73	74	71	73	62	183	106	78	77	81	62



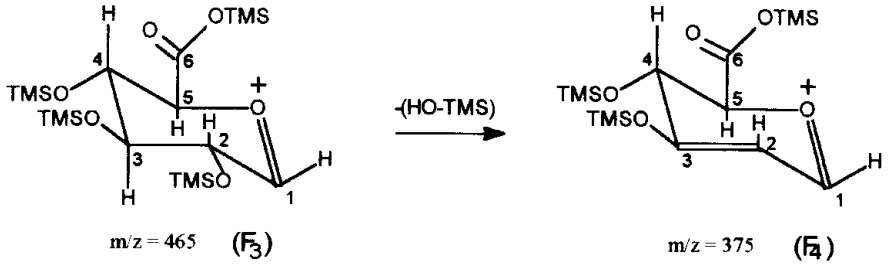
Scheme 3.



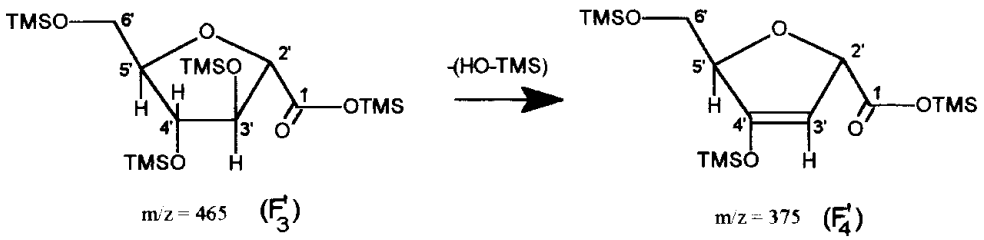
Scheme 4.



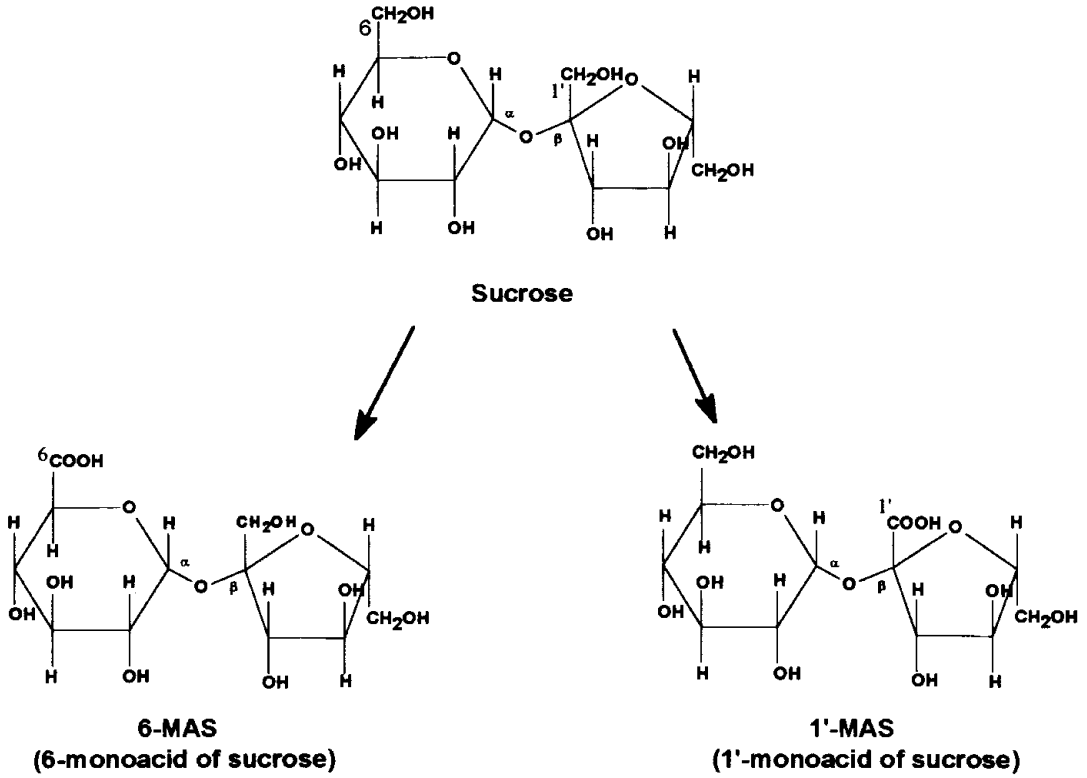
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

437 and 452 may result from a fragmentation pathway involving loss of one or two $^{\cdot}CH_3$. It is well known that the elimination of $^{\cdot}CH_3$ from a $Si(CH_3)_3$ group is favoured when the substituted active hydrogen belongs to a primary alcohol. The fructose moiety displays two primary groups, therefore the fragments F_2'-15 or F_2'-30 are observed:

$(m/z = 451)-{}^{\cdot}CH_3 = (m/z = 436)$
$(m/z = 451)-2({}^{\cdot}CH_3) = (m/z = 421)$
$(m/z = 467)-{}^{\cdot}CH_3 = (m/z = 452)$
$(m/z = 467)-2({}^{\cdot}CH_3) = (m/z = 437)$

while the glucose moiety involves only one primary alcohol:

$(m/z = 451)-{}^{\cdot}CH_3 = (m/z = 436)$
$(m/z = 467)-{}^{\cdot}CH_3 = (m/z = 452)$

The most important fragments in the case of the last three peaks (7, 8 and 9) are observed at $m/z = 375$ and 465. These fragments confirm the presence of a carboxylic group. The localization of this acidic group is not easy to determine, but according to the acid hydrolysis results, fragmentation paths can be proposed for the glucose moiety, see Scheme 6 or, in the case of fructose moiety, see Scheme 7.

3.5. *NMR spectroscopy*

The chemical shifts of the ^{13}C NMR spectrum recorded in D_2O with methanol as an internal reference and in the presence of NaOH in order to keep the pH in the alkaline range and to prevent the lactone formation are given in Table 2.

The confirmation of the oxidation of the primary hydroxyl group located at C_1' into a carboxylic acid group is based on the two peaks (62 and 63 ppm) in the (CH_2OH) region and on the peak at 183 ppm in the 'carbonyl region' of the spectrum. This is in accordance with the interpretation of Eyde *et al.* [6].

4. Conclusion

Although the two main reaction products (i.e., the sucronic acids) are actually not available, the results obtained here have shed new insight into the electrocatalytic oxidation of sucrose. The analytical procedures developed allowed us not only to clearly identify the reaction products, but also to follow quantitatively the reaction pathways.

The analytical results are in agreement with the experimental number of electrons involved during prolonged electrolyses of sucrose, which were found to be very close to 4. This confirms that the oxidation of one primary alcohol group leads to one carboxylic acid group (which needs four electrons per alcohol group), either the 1′-MAS with a selectivity close to 80% or to the 6-MAS (with a selectivity close to 10%) on a upd-Pb/Pt electrode. See Scheme 8.

It can be positively concluded that: (i) high yields can be achieved in long term electrolyses of carbohydrates in aqueous solutions, carried out at a controlled potential, and (ii) using the modern concepts of modified electrodes a controlled orientation of the reactions can lead to high selectivities, which opens up new possibilities for fine and clean chemistry.

Acknowledgements

The authors are very grateful to the 'Groupement Sucrochimie' for its financial support and to the

Comptoir Lyon Alemand Louyot (Paris) for lending us the Pt/Ti electrode.

References

[1] K. B. Kokoh, J.-M. Léger, B. Beden, H. Huser and C. Lamy, *Electrochim. Acta* **37** (1992) 1909.
[2] P. Parpot, PhD Thesis, University of Poitiers, France (1993).
[3] P. Parpot, K. B. Kokoh, B. Beden, E. M. Belgsir, J.-M. Léger and C. Lamy,, *in* 'Heterogeneous Catalysis and Fine Chemicals III' (edited by M.Guisnet *et al.*), Studies in Surface Science and Catalysis, **79** (1993) pp. 439–45.
[4] K. B. Kokoh, P. Parpot, E. M. Belgsir, J.-M. Léger, B. Beden and C. Lamy, *Electrochim. Acta* **38** (1993) 1359.
[5] D. E. Court, PhD, Thesis, University of Southampton, England (1984).
[6] L. A. Edye, G. V. Meehan and G. N. Richards, *J. Carbohydr. Chem.* **10** (1991) 11.
[7] E. M. Belgsir, E. Bouhier, H. Essis Yei, K. B. Kokoh, B. Beden, H. Huser, J.-M. Léger and C. Lamy, *Electrochim. Acta* **36** (1991) 1157.
[8] R. S. Tipson, 'Infrared Spectroscopy of Carbohydrates; A Review of the Literature, US Department of Commerce, NBS Monograph, 110, Washington (1968).
[9] C. C. Sweeley, R. Bentley, M. Makita and W. W. Wells, *J. Amer. Chem. Soc.* **85** (1963) 2479.
[10] D. C. Dejongh, J. D. Hribar, S. Hanessian and P. W. K. Woo, *ibid.* **89** (1967) 3364.
[11] D. C. Dejongh, T. Radford, J. D. Hribar, S. Hanessian, M. Bieber, G. Danson and C. C. Sweeley, *ibid.* **91** (1969) 1728.