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Oxidized glucosidic oligomers: a new class of sequestering agents — preparation and properties

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Oxidized polyglucosides obtained from starch, cellulose or dextrins have very interesting properties as calcium sequestrants and are potentially useful as tripolyphosphate substitutes in detergent formulations. Unfortunately, they are poorly biodegradable. On the other hand, oxidized polyglucosides of lower molecular weight, easily obtainable from starch or dextrins via enzymatic hydrolysis and successive oxidation with sodium hypochlorite are biodegradable and retain sequestering properties.

In the present work, we compare first of all the sequestering properties and biodegradability of oxidized starch, dextrins, glucosidic oligomers and maltotriose. Oxidation has been achieved in all cases with sodium hypochlorite. However, well-defined molecular structures have also been prepared by oxidation of starch and dextrins in two steps with sodium periodate and sodium chlorite, respectively. The products obtained have been compared with the corresponding ones obtained by oxidation with sodium hypochlorite and gave similar results. In fact, sodium hypochlorite oxidizes hydroxyls mainly on the carbon atoms in position 2 and 3 of the glucosidic units, even if with much less selectivity than periodate + chlorite. The reactivity properties of the organic substrates with sodium hypochlorite are in the order maltotriose/dextrins/starch with a ratio of 20/3/1.

Oxidation occurs at alkaline pH, and pH = 8 is optimal for the reaction rate. At this pH, we studied the kinetics of the dextrin oxidation and the hypochlorite decomposition occurring simultaneously.

NOTATION

[Ca]	Calcium ion concentration (mols/litre)
$[\mathrm{Ca}]_\mathrm{o}$	Initial calcium ion concentration (mols/litre)
[CaL]	Concentration of sequestered calcium
C_G	Concentration of the glucosidic units at time t (mols/litre)
C_G^o	Concentration of the glucosidic unit at $t = 0$ (mols/litre)
C_X	Concentration of specie X at time t (mols/litre)
C_X^o	Concentration of specie X at $t = 0$ (mols/litre)
C_Cl^g	Concentration of generated Cl^- (mols/litre)
C_M	Concentration of calcium acetate titrant (mols/litre)
g	Sample weight (g)
K_a	Equilibrium dissociation constant for HClO
K_b	Equilibrium dissociation constant for G—COOH
K'_Ca	Apparent stability constant of calcium complexes
K_d	Kinetic constant for the decomposition reaction of NaClO (litres/(mol min))
K_o	Kinetic constant for the oxidation of a substrate with NaClO (litres/(mol min))
K_w	Equilibrium dissociation constant for H_2O
[L]	Concentration of sequestering active sites
M_w	Average molecular weight of the oxidated glucosidic units (g/mol)
t	Time (mins)
V_a	Volume of 1·593 M NaClO added at $t = 0$ (litres)
V_o	Volume of H_2O initially added (litres)
V_s	Volume of the solution at $t = 0$ (litres)
V_t	Volume of the added titrant (litres)

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INTRODUCTION

Sodium tripolyphosphates (STPP) have been used for many years as sequestering builders in detergent formulations. Now phosphates are banned in many countries, since they are responsible for water eutrophication (Chiaudani *et al.*, 1988). As a result, an intensive search is operative worldwide in order to find phosphate substitutes. These products must have good sequestering properties towards both calcium and magnesium, must be biodegradable, non-toxic and of low cost.

Up to now, the phosphate substitutes of commercial interest are the complexing agents nitrilotriacetic acid and citric acid, a calcium precipitating agent such as sodium carbonate and an inorganic ionic exchanger such as zeolite NaA. These compounds and their mixtures are normally employed in washing powders (Matzner *et al.*, 1973, Crutchfield, 1978), but their performances are not completely satisfactory. Zeolites, for example, exchange magnesium slowly, thus requiring the presence of small amounts of very efficient sequestering agents such as maleic anhydride and acrylic acid copolymers. These copolymers are non-biodegradable, and accumulate in the sludges with unknown effects on biological life. Moreover, zeolites are insoluble powders and can obstruct pipes.

Nitrilotriacetic acid has a high sequestering efficiency and is readily biodegradable, but the presence of nitrogen in the molecule could produce teratogenic effects (Kemper *et al.*, 1975). Therefore, its use as a builder is banned in many countries. Citric acid has low efficiency and is, therefore, employed as a builder additive only. The drawbacks shown by the phospate substitutes of commercial interest have stimulated the search for new sequestering organic builders with the following properties: molecules of low molecular weight, containing only carbon, oxygen and hydrogen, being readily biodegradable, non-toxic and showing a high sequestering activity, easy to prepare and of low cost.

Kemper *et al.* (1975) and Crutchfield (1978) synthesized and tested several ether carboxylates but obtained good results only for a few compounds, particularly in regard to biodegradability. They indicated the carboxylic group with an ether oxygen located on the α carbon atom as the best ligand; on the other hand, alcohol or acetal oxygen should be less efficient. Despite this conclusion, Nieuwenhuizen *et al.* (1983) showed that oxidized carbohydrates containing acetal oxygens and carboxilic groups as main ligands have higher dentate ligands favouring calcium sequestration strength. Acetals have the advantage of being relatively stable in alkaline media and to decompose in acid media. This means that acetal compounds are stable during the washing process, but are hydrolysed in the acidic waste water. Decomposition before biological degradation accelerates full degradation of these compounds (Nienwenhuizen *et al.*, 1983). According to Nieuwenhuizen *et al.* (1983) the sequestering capacity of low molecular weight oxidized carbohydrates increases by increasing the molecular weight. Floor *et al.* (1989) have shown that above a critical value of the carboxyl content, more effective calcium complexing sites are created.

It is also known that oxidized starch and dextrins, i.e. high molecular weight carbohydrates, are poorly biodegradable (Diamantoglou, *et al.*, 1977*a*). Therefore, the molecular weight of the oxidized carbohydrates must be high enough to give satisfactory sequestering capacity without losing the degradability properties.

More recently, Santacesaria *et al.* (1991) prepared and tested oxidized carbohydrates with these properties. These compounds were obtained by hydrolysis of commercial dextrins in the presence of α-amylase and by subsequent oxidation of the obtained oligosaccharides, the average molecular weight of which corresponds to 3–4 glucosidic units.

The methods applied for the preliminary enzymatic hydrolysis and the results obtained such as oligomer distributions are described in the present work, together with the methods used for oxidation of the hydrolysed carbohydrates.

The properties of the obtained products such as sequestering capacity and biodegradability are determined and compared with those of oxidized carbohydrates of higher molecular weight, i.e. oxidized starch or dextrins.

Oxidation has been performed mainly with sodium hypochlorite but sometimes with the more selective periodate + chlorite in order to have the regular structure molecules useful as a reference.

The kinetic and mechanicistic aspects involved in the oxidation performed with hypochlorite have been considered and the calcium sequestration stoichiometry of about 1 Ca:4 carboxylic groups has been confirmed (Casu *et al.*, 1984*a*; Nieuwenhuizen, 1985).

EXPERIMENTAL

Enzymatic hydrolysis of dextrins

Enzymatic hydrolysis of dextrins has been performed by using α-amylase from *Bacillus Subtillis*. Generally, 30 g of a commercial maltodextrin of the type Snowflake 1911 obtained from enzymatic wet treatment of maize starch are dispersed in 500 cm^3 water and heated at 40–45°C until completely dissolved. Then, 125 cm^3 of 0·1 M KCl solution and 0·01 M CH_3COOK are added. To this solution, 90 mg (50 units/mg) of the enzyme α-amylase are added. The reaction was prolonged at 45°C for 4 h and at room temperature for about 10 h.

The solution was then analysed by HPLC, using a Lichrosorb RP-18 (10 μm) column and water as mobile phase (0·8 cm^3/min).

It is well known that α-amylase breaks carbohydrate molecular chains with a random action and in an endo-manner (Radley, 1968). Therefore, starting from a commercial dextrin of the type Snowflake 1911 (Sautacesaria *et al.*, 1991), oligomers with 2–8 glucosidic units and with distribution maxima around 3–4 units were obtained.

Oxidation procedures

Carbohydrates have been oxidized with sodium hypochlorite or in two steps with sodium periodate and sodium chlorite. In the last case, we obtained a reference structure because, as is well known (Casu *et al.*, 1984*a*), periodate shows good selectivity in giving dialdehyde on carbons 2 and 3 of the glucosidic unit. Then, chlorite easily osidizes aldehydic groups to carboxylic ones. These structures are a useful reference for the products obtained with the much less selective hypochlorite.

We have achieved oxidations with hypochlorite on substrates differing in molecular weight, i.e. starch, dextrin, hydrolysed dextrin (amylase-treated dextrins) and maltotriose. Molecular weights are about 10^6 for starch, about 8000 for the commercial dextrin, about 700 for the hydrolysed dextrin and 540 for maltotriose, all in the native form and calculated by multiplying the average number of glucosidic units in the chain by the molecular weight of each unit.

The oxidation via periodate + chlorite was mainly performed on starch and dextrin. An example of the procedure applied is as follows: 18 g carbohydrate were dispersed in 100 cm^3 water, then 30 g sodium periodate dissolved in 400 cm^3 water were added. Reactants must be taken for 24 h at 15–20°C in the dark. The dialdehyde obtained was completely precipitated with alcohol or acetone. Then, the precipitate was washed with alcohol or acetone and dried. A weighed sample of dialdehyde, for example 8 g, was dispersed in 220 cm^3 of a solution containing 22·6 g sodium chlorite with 6·5 cm^3 acetic acid. The reaction occurred for 24 h at room temperature, under nitrogen (Casu, *et al.*, 1984*a*), then the solution was fluxed with nitrogen to eliminate residual chlorine and the final product precipitated with ethanol, filtered and dried under vacuum.

An example of oxidation with sodium hypochlorite is as follows: 10 g carbohydrate powder were dispersed or dissolved in 100 cm^3 water. Ten cm^3 of commercial sodium hypochlorite containing 8–13% by weight of chlorine were added at first at room temperature. Then, the pH was adjusted with concentrated HCl at a value of 8. It rapidly decreased because of the effect of the reaction oxidation but also of the sodium hypochlorite decomposition. We kept pH = 8 almost constant by adding small amounts of hypochlorite to compensate for both the above-mentioned effects. Normally, 200–300 cm^3 of hypochlorite are added in this way, corresponding to a final molar ratio between the oxidant and the glucosidic units of about 5. A molar ratio higher than the stoichiometric one is necessary as hypochlorite rapidly decomposes under the described conditions. When all the prefixed quantities of hypochlorite had been added, the pH was kept constant by adding NaOH. The run was interrupted at negligible values of residual chlorine. The chlorine concentration was determined by iodometric titration.

The oxidized carbohydrates obtained having high molecular weight (starches, dextrins) were precipitated with alcohol, filtered and dried, while in the other cases the products were dried directly in a rotavapor and collected with the large quantity of sodium chloride obtained in the occurring reactions.

The described procedure is necessary because the oxidation reaction rate attains its maximum at pH = 8 (Diamantoglou, 1977*b*) and carbohydrates are stable to hydrolysis in those conditions. A kinetic study has been carried out on the oxidation with hypochlorite by measuring the amount of hypochlorite added during the time while the pH was kept constant, and the evolution with time of the residual chlorine. The same kinetic runs were performed in the absence of the organic substrate in order to evaluate the contribution of decomposition to hypochlorite consumption. Kinetic runs were performed at different temperatures and on carbohydrates of different molecular weights.

Methods for determining sequestering power

The sequestering power, SP, usually expressed as mg $CaCO_3$ per g of sequestering agent, was determined by two different methods. In the first, a membrane electrode reversible to calcium concentration was applied (Craggs *et al.*, 1979), consisting in titration of a sequestrant solution with calcium acetate. The second method consists in the same titration in the presence of sodium carbonate up to turbidity (Kemper *et al.*, 1975; Crutchfield, 1978). Turbidity occurs as a consequence of calcium carbonate precipitation when the solubility equilibrium concentration $Ca^{++} = 5 \times 10^{-4}$ M is reached. The membrane electrode used is an AMEL 201/Ca while a calomel electrode from the same company has been used as the reference electrode.

Method for determining biodegradability

Samples of oxidized carbohydrates were submitted to both Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) tests. COD was determined following a standard procedure (C.E.E., 1984) consisting in the oxidation of the organic sample dissolved in water with a solution of potassium bicromate and sulphuric acid in the presence of silver sulphate as catalyst. The solution was heated at the boiling point and refluxed for two hours. Unreacted bicromate was titrated with ferrous sulphate.

BOD determination was performed in closed bottles with a standard procedure (C.E.E., 1984) for at least 30 days. The employed method is based on the determination of the oxygen dissolved in the sample before and after incubation at 20°C with an amperometric membrane electrode. The pH of the solution was initially adjusted to within the range 6·5–8·3. The bacterial population used was a mixed one, derived from a municipal waste-water purification plant.

Results obtained for the different oxidized substrates were compared by determining the percent of biodegradation, i.e.

$$\text{Biodegradation} = \frac{\text{BOD}}{\text{COD}} \times 100\%$$

Other techniques applied, reagents

The samples of oxidized carbohydrates were subjected to titrations to determine the number of carboxylic groups per glucosidic unit. These titrations were performed by introducing a weighed amount of the sample, e.g. 0·1 g, in 100 cm^3 water. Then, 0·1 M HCl was added until pH = 1·5 was reached, the excess acid having been determined by potentiometric titration with 0·1 M NaOH.

The samples of oxidized carbohydrates have also been subjected to ^{13}C NMR analysis with a Bruker WH 270 spectrophotometer. Trimethylsilylpropionic acid d_4 sodium salt (TSP) was used as internal reference. The samples was dissolved in D_2O before the analysis. The products obtained via the periodate + chlorite oxidation confirm the NMR spectra recently published by Casu *et al.* (1984*b*) and are useful as a reference for the other samples examined.

Starches and dextrins used were supplied by Novamont SpA, while other reagents were produced by Carlo Erba SpA at the maximum level of purity available.

RESULTS AND DISCUSSION

Preparation and characterization of carbohydrates oxidized with hypochlorite

Oxidation runs with sodium hypochlorite have been performed on carbohydrates of different molecular weights such as starch, dextrins, hydrolysed dextrins and maltotriose. Oxidation runs have been performed with periodate + chlorite on starch and dextrin only. In Table 1, sequestering powers (SPs) obtained for oxidized carbohydrates of different average molecular weights are reported. Products obtained by oxidation with NaClO at 20°C with a NaClO/glucosidic units molar ratio of 5 are compared with the products obtained by oxidation with periodate + chlorite. As it can be seen, the SP increases by decreasing the molecular weight of the organic substrate. The products obtained through periodate + chlorite oxidation show an SP comparable to or slightly lower than that obtained by hypochlorite.

More significant are the plots shown in Fig. 1, which shows the calcium ion concentrations determined during the titration of 0·3 g of different oxidized carbohydrates with 0·1 M calcium acetate. Calcium ion concentrations have been determined with the above-mentioned membrane electrode. In the same plot, the behaviour of EDTA is shown for comparison purposes. As can be seen, oxidized starch and dextrin show a progressive increase in calcium ion concentration, while hydrolysed dextrin and maltotriose, i.e. the products with lower molecular weight, show a sharp initial increase of calcium ion concentrations, followed by another smooth and progressive rise. The behaviour of the high molecular weight carbohydrates can be explained by assuming the presence of carboxylic groups of different SPs. It is also worth mentioning that the samples oxidized with periodate + chlorite show the same behaviour. Therefore, we must conclude that either the structure regularity has no influence in determining the sequestration properties of the molecules or that the samples obtained via hypochlorite are regular enough to give a similar behaviour. As will be seen, the second hypothesis is more reliable. In the case of low molecular weight, regularity is lost as the oxidation degree is normally higher, for example the contribution of the terminal carboxylic group originating from the oxidation of the aldehydic terminal group becomes more important by decreasing the molecular weight (Radley, 1968). Therefore, in these cases we have an initially rapid disappearance of carboxylic groups with high SP and then a progressive disappearance of the

Table 1. Sequestering powers and average number of carboxylic groups per glucosidic unit obtained for oxidized carbohydrates of different average molecular weight. Oxidation has been performed in one step with NaClO or two steps with periodate + chlorite

Substrates	Type of oxidation	Sequestration power (mg CaCO_3/g)	Oxidation degree from titration	Oxidation degree from SP data
Starch	NaClO	245	2·3	2·6
Dextrin	NaClO	260	2·2	2·7
Hydrolized dextrin	NaClO	275	2·3	2·9
Maltotriose	NaClO	285	2·0	2·8
Starch	$IO_4^- + ClO_2^-$	175	—	—
Dextrin	$IO_4^- + ClO_2^-$	230	2·1	2·4

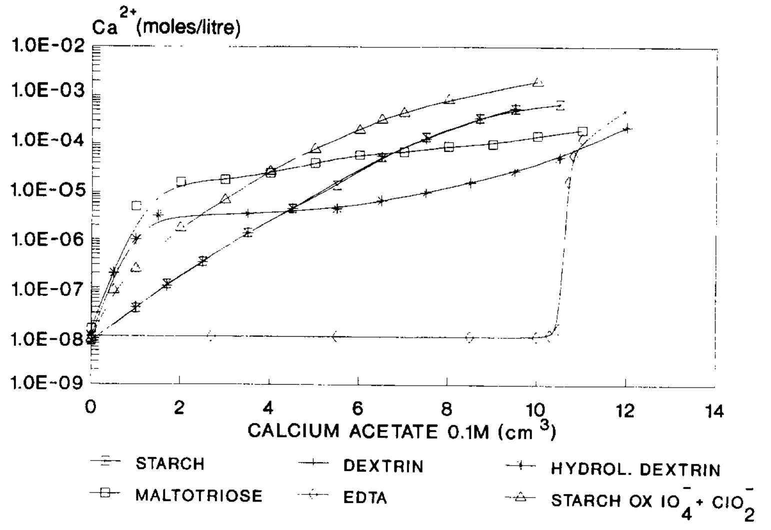


Fig. 1. Calcium concentration determined with a reversible membrane electrode in the titration of 0·3 g of different oxidized carbohydrates with calcium acetate 0·1 M. All the carbohydrates were oxidized with NaClO, with the exception of starch, which was also oxidized with periodate. EDTA behaviour is also reported for comparison.

others. However, after this sharp increase in calcium concentrations, the concentration remains low enough for practical use as a builder.

This aspect can be seen better in Fig. 2 where a calcium solution is titrated with a solution of the sequestering agent. Calcium concentrations are shown in this plot as water hardness (mg CaO/100 g of sequestering agent). In the same figure, the performance of sodium tripolyphosphate is reported for comparison purposes. As can be seen, the performances of the oxidized carbohydrates in reducing water hardness are satisfactory for all samples tested and the hardness obtainable with 1–2 g/litre of the organic sequestering agent is suitable for detergents (Crutchfield, 1978).

In addition, it follows from Fig. 2 that the addition of more than 1–2 g/litre of sequestering agent is not useful, because the calcium concentration remains at about the same level. From the SP data it is possible to evaluate the oxidation degree, i.e. the average number of carboxylic groups per glucosidic unit if the stoichiometry of the calcium complexation reaction is known. The same result can be achieved by determining the number of carboxylic groups by potentiometric titration, as already described. For the calcium complexation stoichiometry we found that the suggestions of Casu *et al.* (1984*a*) of 1 Ca:4 COOH is reliable. In Table 1 we also report the oxidation degree determined in the two described ways assuming the stoichiometry

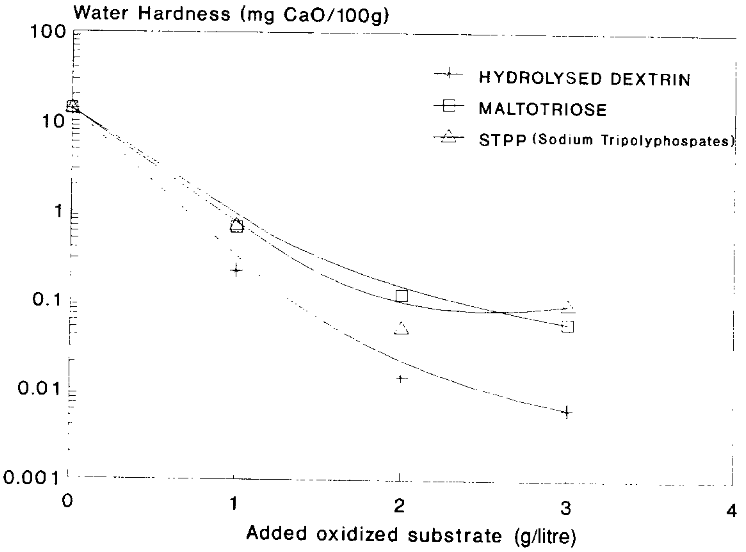


Fig. 2. Decrease in the water hardness following sequestrant addition. All the carbohydrates are in the oxidized form obtained as consequence of the reaction with NaClO. STPP is sodium tripolyphosphate.

suggested by Casu *et al.* (1984*a*). The discrepancies observed in Table 1 must be ascribed to the possibility of a variable stoichiometry. However, it must be noted that the oxidation degree increases with decreasing molecular weight. This aspect will be examined in more detail later.

From data such as those reported in Figs 1 or 2 it is possible to evaluate the apparent stability constants by referring to the glucosidic unit. The calculation procedures adopted are the following:

$$K'_{\mathrm{Ca}} = \frac{[\mathrm{CaL}]}{[\mathrm{Ca}^{2+}] \times [\mathrm{L}]}$$

$$[\mathrm{CaL}] = \frac{C_{\mathrm{M}} V_{\mathrm{t}} - ([\mathrm{Ca}^{2+}] - [\mathrm{Ca}^{2+}]_0) \times (V_{\mathrm{s}} + V_{\mathrm{t}})}{(V_{\mathrm{s}} + V_{\mathrm{t}})}$$

$$[\mathrm{Ca}^{2+}] = \text{measured calcium ion concentration}$$

$$[\mathrm{L}] = \frac{g}{M_{\mathrm{w}} (V_{\mathrm{s}} + V_{\mathrm{t}})} - \frac{C_{\mathrm{M}} V_{\mathrm{t}} - ([\mathrm{Ca}^{2+}] - [\mathrm{Ca}^{2+}]_0 (V_{\mathrm{s}} + V_{\mathrm{t}})}{(V_{\mathrm{s}} + V_{\mathrm{t}})}$$

where g is the oxidized carbohydrate sample weight and M_{w} the average molecular weight of the oxidated glucosidic unit, that is variable with the oxidation degree. Therefore, [L] is the molar concentration of the oxidized glucosidic units existing in the solution. With the replacement of these expressions in the first equation above and considering $[\mathrm{Ca}^{2+}]_0 \approx 0$, we obtain

$$K'_{\mathrm{Ca}} = \frac{C_{\mathrm{M}} V_{\mathrm{t}} - [\mathrm{Ca}^{2+}] * (V_{\mathrm{s}} + V_{\mathrm{t}})}{[\mathrm{Ca}^{2+}] * \{g/M_{\mathrm{w}} - C_{\mathrm{M}} V_{\mathrm{t}} - [\mathrm{Ca}^{2+}] * (V_{\mathrm{s}} + V_{\mathrm{t}})\}}$$

With this expression it is possible to calculate K'_{Ca} values for any experimental point. We can therefore plot log K'_{Ca} as a function of the moles of Ca^{2+} for each glucosidic unit as reported in Fig. 3 for all samples of oxidized carbohydrate.

As can be seen, all log K'_{Ca} values are in the range 4·2–6·5. In particular, we show the possibility of the existence of sequestering sites of different strength on oxidized starch and dextrin. Sites with higher log K'_{Ca} react preferentially and are, therefore, neutralized first. In the case of both high and low molecular weight, a limiting value of log $K'_{\mathrm{Ca}} \approx 4{\cdot}2$ is reached.

^{13}C-NMR spectra have been performed, respectively, on a dextrin oxidized with periodate + chlorite and with hypochlorite. Results obtained in the first case are quite similar to those reported by Casu *et al.* (1984*a*) on amylose. In Table 2 the chemical shifts obtained for the different carbon atoms of the samples oxidized with periodate + chlorite and hypochlorite respectively are reported and compared with those given by Casu *et al.* (1984*b*).

It must be concluded that periodate is highly selective in oxidizing hydroxyls at the carbon atoms in positions 2 and 3 while hypochlorite is certainly much less selective but preferentially oxidizes hydroxyls in the same position. This fact well explains the similarity in the sequestering action of the products obtained with the two different oxidants. Finally, all samples have been submitted to biodegradability tests and the results obtained are reported in Table 3. As can be seen, biodegradability of the oxidized polysaccharides increases as the average molecular weight decreases. A citric acid biodegradability test has been introduced as a useful comparison.

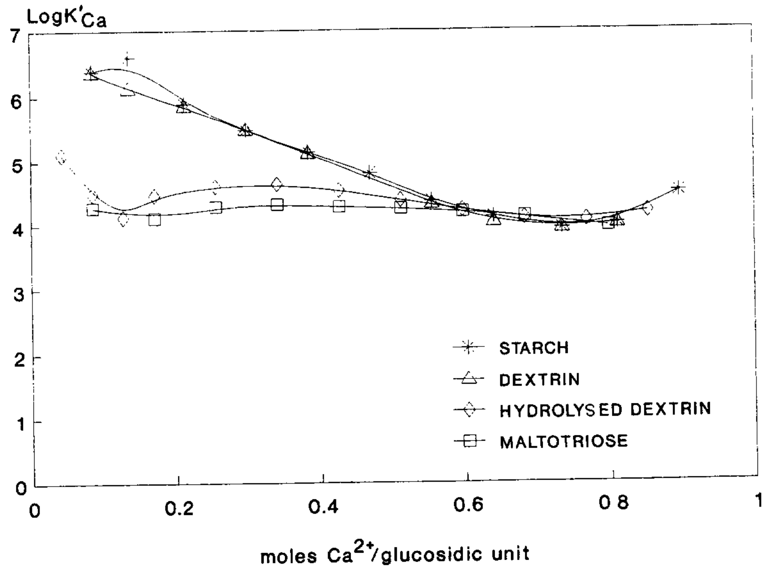
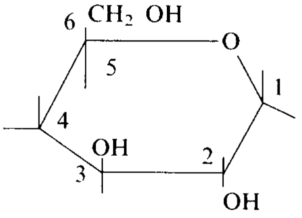


Fig. 3. Apparent stability constants for calcium ion complexes in different substrates oxidized with NaClO, as a function of the oxidation degree. K'_{Ca} is referred to the glucosidic unit.

Table 2. The chemical shifts from the ^{13}C NMR spectrum of oxidized starch (A) and dextrin (B and C). Chemical shifts (ppm)

	A	B	C
C − 1	101·2	102·98	102·84
C − 2	177·1	178·80	179·86
C − 3	175·4	177·80	178·05
C − 4	80·7	82·83	80·32
C − 5	78·8	80·22	67·14
C − 6	62·1	68·40	65·68



A: Casu *et al.* (1984*b*).
B: Oxidation with $IO_4^- + ClO_2^-$.
C: Oxidation with NaClO.

Table 3. A 30-day biodegradability test performed on different carbohydrates oxidized with NaClO. Citric acid as also been tested for comparison purposes

	BOD/COD (%)
Starch	<3
Dextrin	10
Hydrolized Dextrin	50
Maltotriose	60
Citric acid	70

Kinetics and mechanisms in the oxidation of polyglucosides with hypochlorite

Sodium hypochlorite is a strong oxidizing agent. Its oxidizing capacity changes with pH because of a change in the oxidizing specie as a consequence of the following equilibria (McKillican & Purves, 1954):

$$NaClO + H_2O \rightleftharpoons HClO + NaOH \quad (1)$$

$$HClO \rightleftharpoons H^+ + ClO^- \quad (2)$$

$$HClO + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O \quad (3)$$

Therefore, Cl_2 prevails in an acidic environment, ClO^- in an alkaline medium and HClO in neutral conditions. The evolution of the percent concentrations of these species as a function of pH, calculated on the basis of the equilibrium constants involved, is shown in Fig. 4. For the oxidation of carbohydrates, moderately alkaline solutions (pH = 7–9) are preferred in order to prevent the formation of chlorates (Whistler & Schweiger, 1957):

$$3\ NaClO \longrightarrow 2\ NaCl + NaClO_3 \quad (4)$$

and because oxidation reaction rates are higher in this pH range, as can be seen from the plot of Fig. 5 (Nevel, 1963). The reaction temperature must be as low as possible to reduce the formation of chlorates and the decomposition of hypochlorite. Hypochlorite decomposition is rather fast in the described conditions; therefore, in order to obtain the desired yield, an excess of hypochlorite must be used. To define correctly the amount of hypochlorite necessary to oxidize a given quantity of carbohydrate to a certain level, both the kinetics of oxidation and hypochlorite decomposition must be known.

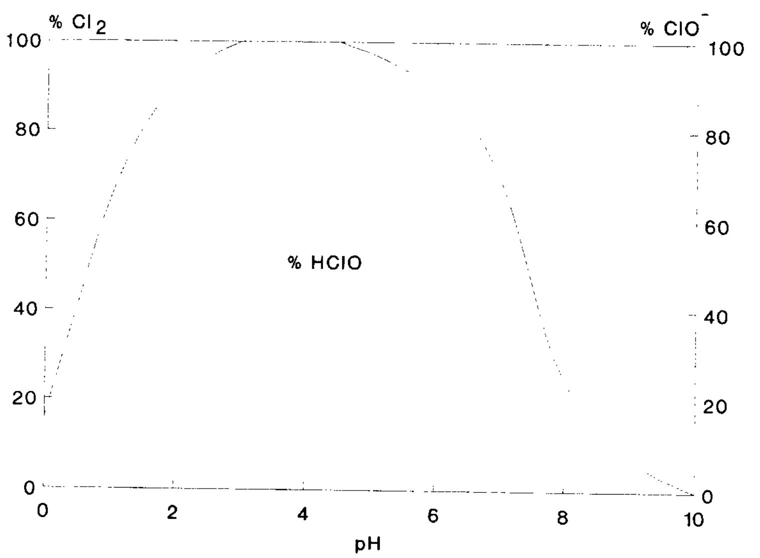


Fig. 4. Percent concentration in water of Cl_2–HClO–ClO^-, respectively, at different pH values, calculated on the basis of the chemical equilibria constants, at 25°C (Casu *et al.*, 1984*b*).

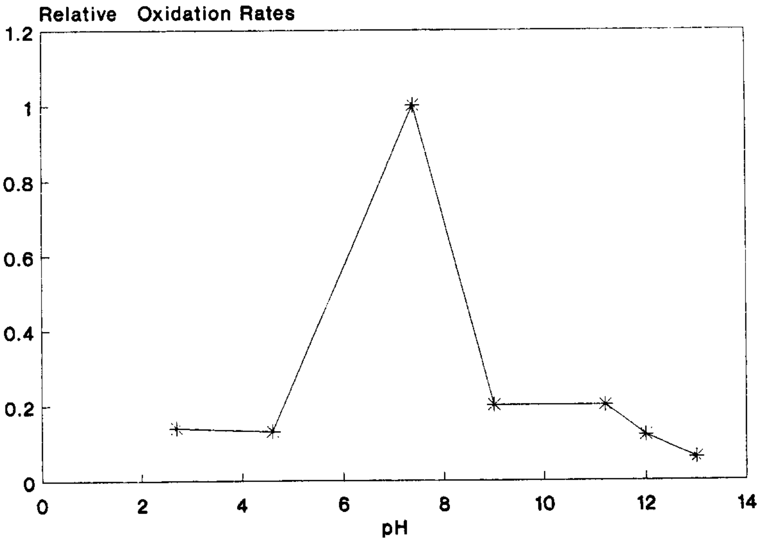


Fig. 5. Relative oxidation rates obtained for starch in the presence of NaClO at different pH values (Whistler and Schweiger, 1957).

Oxidation kinetic runs have been performed on different substrates such as starch, dextrins and maltotriose.

Other kinetic runs have been performed on dextrin at different temperatures and pHs. The procedure adopted in all the kinetic runs performed is the following: a weighed sample of carbohydrate, usually 10 g, is dispersed in 100 cm^3 of distilled water. Then 10 cm^3 of commercial sodium hypochlorite (chlorine concentration <12% by weight) are added. The pH is adjusted to the desired value with a few drops of concentrated hydrogen chloride. The pH decreases as a consequence of both the oxidation reaction and the hypochlorite decomposition. The pH has then been kept constant by adding, when necessary, small amounts of hypochlorite until a predetermined ratio of hypochlorite moles/glucosidic unit moles is reached. Usually, this ratio is taken as about 5. When the hypochlorite is completely added to the preparation, the pH is kept constant with the addition of concentrated NaOH; the residual chlorine in the solution is determined at different times by withdrawing small samples of the reacting solution. We know the volume and concentration of the hypochlorite added with time for a given pH, temperature and substrate, followed by the evolution with time of the residual chlorine. In order to interpret the kinetic data, it is necessary to know the relative contribution of the oxidation reaction and hypochlorite decomposition to the hypochlorite consumption, remembering that both reactions affect the solution pH. For this reason, we have also studied the kinetics of hypochlorite decomposition. In this case, kinetic runs have been performed by adding to 100 cm^3 water a predetermined amount of sodium hypochlorite and by adjusting the pH with concentrated HCl. Small samples have been withdrawn at different times and residual chlorine in the samples has been titrated iodometrically. Kinetic results obtained at different temperatures are reported in Fig. 6. It is interesting to observe that hypochlorite decomposition in such conditions occurs much faster than reported in previous literature (Lister, 1956).

In Fig. 7, the kinetic behaviours observed for different polysaccharides are reported. As it can be seen, oxidation reaction rates strongly increase as the molecular weight decreases in agreement with the molar concentration increase. In Fig. 8, the effect of pH on the oxidation rate of a dextrin is shown. The highest rates are at pH 8. For this reason, the kinetic study has been performed at this pH value. Oxidation kinetic runs on dextrin were performed at different temperatures, and an example is shown in Fig. 9. The interpretation of the runs of Figs 6 and 9 requires the development of suitable kinetic models for hypochlorite decomposition and dextrin oxidation.

Hypochlorite can decompose giving both chlorides or chlorates (Lister, 1952, 1956; Morris, 1966). Here we do not distinguish between the two possible reaction paths and in agreement with the suggestion of the literature, we assume a second-order kinetic law; therefore

$$r_d = -\frac{dC_{NaClO}}{dt} = K_d\, C^2_{NaClO} \quad (5)$$

where C_{NaClO} is the NaClO concentration at time t. By integrating eqn (5), eqn (6) is obtained:

$$C_{NaClO} = C^o_{NaClO}/(1 + k_d\, C^o_{NaClO}\, t) \quad (6)$$

where C^o_{NaClO} is the initial concentration of NaClO. Kinetic parameters, related to K_d, obtained by regression on the experimental data are reported in Table 4.

These parameters allow a good fit to the data, as shown in Fig. 6.

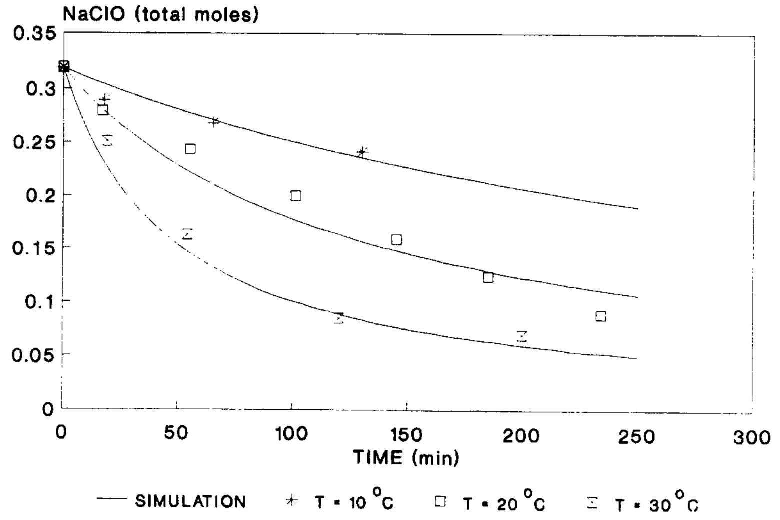


Fig. 6. Decomposition of NaClO as a function of time, at different temperatures.

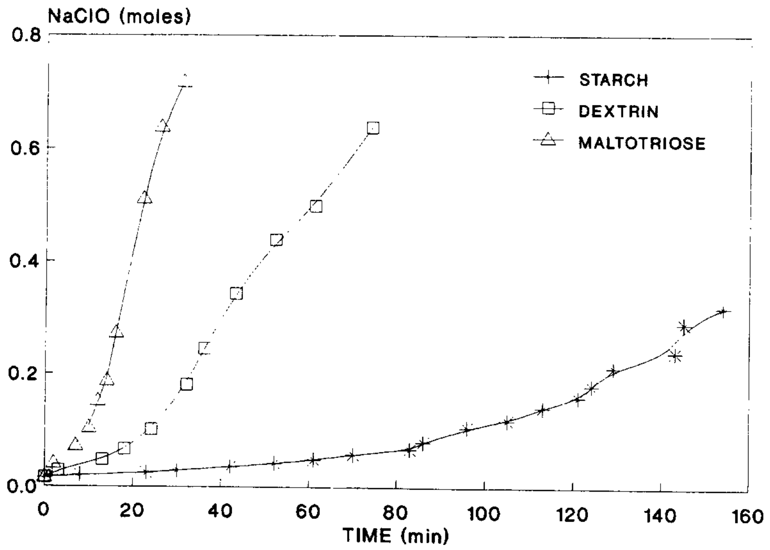


Fig. 7. Hypochlorite consumption at pH = 8 with time for different organic substrates.

In the oxidation runs decomposition also occurs. Hypochlorite is consumed from both of the following reactions:

$$2\ \text{NaClO} \xrightarrow{r_d} 2\ \text{NaCl} + \text{O}_2 \qquad (7)$$

$$3\ \text{NaClO} + \text{G} \xrightarrow{r_o} 3\ \text{NaCl} + \text{G(COOH)}_2 + \text{H}_2\text{O} \qquad (8)$$

where G is the glucosidic unit of the organic substrate, and r_d and r_o are the reaction rates for reactions (7) and (8), respectively. The stoichiometry of reaction (8) reflects the observation that hypochlorite mainly oxidizes carbon atoms in positions 2 and 3 of the glucosidic units, giving two carboxilic groups. It is reasonable to suppose that other possible oxidations are slower.

Considering reaction (7) and (8) together results in the following stoichiometric matrix:

i j	NaClO	NaCl	G	G(COOH)$_2$	H$_2$O	O$_2$
7	−2	2	0	0	0	1
8	−3	3	−1	1	1	0

(9)

where j are the reaction indices and i the components ones; consequently, the reaction rates of disappearing reagents and formed products are, respectively:

$$\begin{aligned} r_{\text{NaClO}} &= -2\,r_d - 3\,r_o \\ r_{\text{NaCl}} &= 2\,r_d + 3\,r_o \\ r_{\text{G}} &= -r_o \\ r_{\text{G}}(\text{COOH})_2 &= r_o \end{aligned} \qquad (10)$$

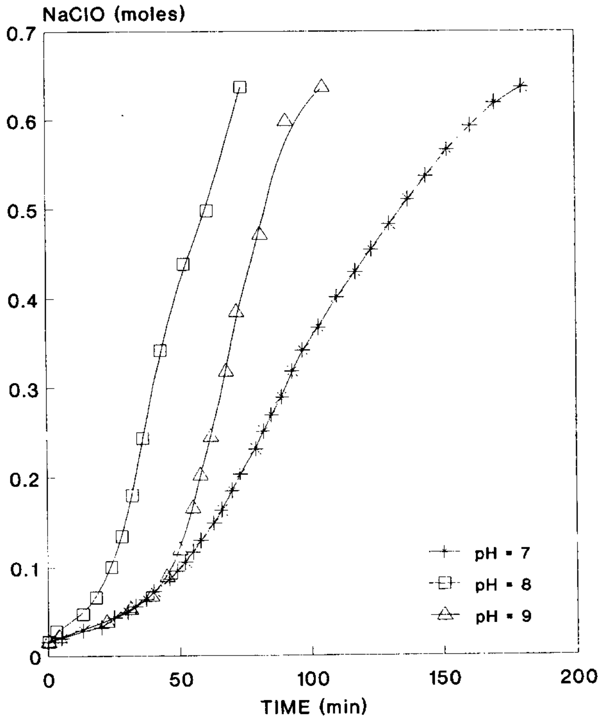


Fig. 8. Effect of pH on the hypochlorite consumption in the oxidation of a commercial dextrin.

We have already seen that a second-order kinetic law will reproduce the experimental data for r_d (eqn (5)). In the case of r_o, we assumed, as a first approximation, a kinetic law of the type

$$r_o = k_o C_{NaClO} C_G \tag{11}$$

It is useful to define a normalized oxidation degree as

$$g_o = \frac{n_{COOH}/\text{glucosidic unit}}{2} \tag{12}$$

where n_{COOH} is the number of carboxylic groups in moles. In this case

$$C_G = C_G^o(1 - g_o) \tag{13}$$

consequently

$$\frac{dg_o}{dt} = k_o C_{NaClO} C_G^o (1 - g_o) \tag{14}$$

The rate at which NaClO disappears would be

$$\begin{aligned} r_{NaClO} &= -\frac{d C_{NaClO}}{dt} = -2k_d C_{NaClO}^2 \\ &\quad + 3k_o C_{NaClO} C_G^o (1 - g_o) \end{aligned} \tag{15}$$

Kinetic runs such as the one shown in Fig. 9 have been performed first in semibatch conditions in respect to NaClO and then in batch ones, keeping the pH constant and equal to 8 in both cases. The initial volume conditions are, therefore,

V_o = 100 cm^3 of water

V_a = 10 cm^3 of 1·593 M NaClO

plus a negligible volumetric amount of concentrated HCl. In order to undertake calculations, we must define the initial solution composition. First of all, the NaClO concentration after dilution is

$$C_{NaClO} = \frac{V_a C_{NaClO}^{ms}}{V_a + V_o} \tag{16}$$

where C_{NaClO}^{ms} is the concentration of NaClO in the mother solution. The initial concentration of the organic substrate is calculated as

$$C_G^o = \frac{g}{M_w (V_a + V_o)} = \text{moles of glucosidic units/litre} \tag{17}$$

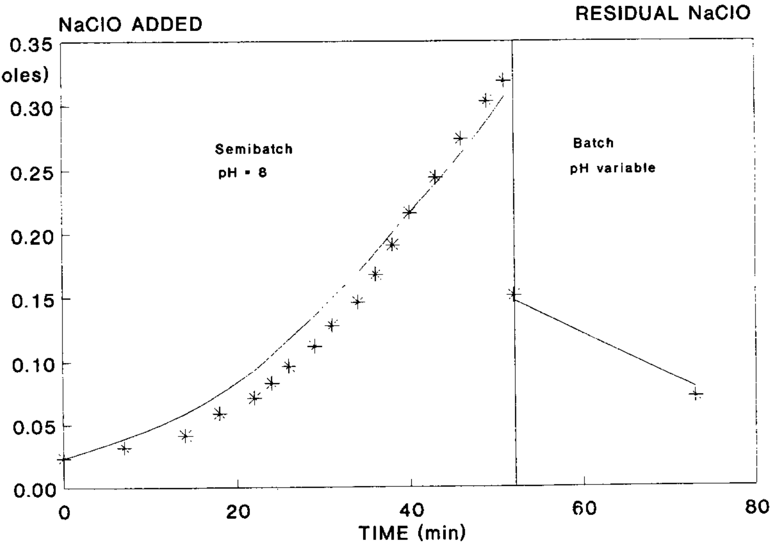


Fig. 9. Hypochlorite consumption in the oxidation of a dextrin, at 20°C, pH = 8. Dots, experimental; lines, calculated.

Table 4. Kinetics parameters obtained for NaClO decomposition and dextrin oxidation

Temperature (°C)	K_o (litres/(mol min))	K_d (litres/(mol min))	K_a	K_w
1	$(6\cdot5 \pm 0\cdot7) \times 10^{-3}$	$(2\cdot0 \pm 0\cdot3) \times 10^{-3}$	$1\cdot5 \times 10^{-8}$	$1\cdot3 \times 10^{-15}$
10	$(8\cdot9 \pm 0\cdot9) \times 10^{-3}$	$(7\cdot5 \pm 0\cdot8) \times 10^{-3}$	$2\cdot04 \times 10^{-8}$	$3\cdot6 \times 10^{-15}$
20	$(2\cdot3 \pm 0\cdot3) \times 10^{-2}$	$(3\cdot1 \pm 0\cdot4) \times 10^{-2}$	$2\cdot6 \times 10^{-8}$	$8\cdot6 \times 10^{-15}$

$K_d = K_d^o \exp(-E_d/RT) = (1\cdot25 \pm 0\cdot25) \cdot 10^{11} \exp((-18\,000 \pm 540)/RT)$.
$K_o = K_o^o \exp(-E/RT) = (2\cdot46 \pm 0\cdot43) \cdot 10^{15} \exp((-22\,600 \pm 750)/RT)$.

The composition of the initial solution at pH = 8 can be calculated by solving the following system of equations:

$$C_{H^+} C_{ClO^-} = K_a C_{HClO} \tag{18}$$

$$C_{H^+} C_{OH} = K_w \tag{19}$$

$$C_{HClO} + C_{ClO^-} = C_{NaClO} = C_{OX} \tag{20}$$

$$C_{Na^+} = C_{OX} \tag{21}$$

$$C_{Cl}^o = C_{HCl} \tag{22}$$

$$C_{H^+} + C_{Na^+} = C_{OH} + C_{ClO^-} + C_{Cl^-} \tag{23}$$

K_a and K_w used in the calculations are given in Table 4. The amount of concentrated HCl necessary to obtain pH = 8 can be determined from eqn (23); thus

$$C_{HCl} = C_{H^+} + C_{OX} - \frac{K_w}{C_{H^+}} - \frac{K_a C_{OX}}{C_{H^+} + K_a} \tag{24}$$

The oxidation of an organic substrate introduces into the solution some carboxylic groups partially dissociated as acids:

$$G-COOH \overset{K_b}{\rightleftarrows} G-COO^- + H^+ \tag{25}$$

in this case, the pH is affected from the presence of NaClO, HClO, G—COON$_a$ and G—COOH all being simultaneously involved in the acid–base equilibria. To determine the composition of the solution at any reaction time, we must solve the following equations system:

$$C_{H^+} C_{OH^-} = K_w \tag{26}$$

$$C_{H^+} C_{ClO^-} = K_a C_{HClO} \tag{27}$$

$$C_{H^+} C_{GCOO^-} = K_b C_{GCOOH} \tag{28}$$

$$C_{GCOOH} + C_{GCOO^-} = 2 g_o C_G^o \tag{29}$$

$$C_{HClO} + C_{ClO} = C_{OX} \tag{30}$$

$$C_{Na^+} = C_{Cl}^g + C_{OX} \tag{31}$$

$$C_{Cl} = C_{Cl^-}^o + C_{Cl^-}^g \tag{32}$$

$$C_{H^+} + C_{Na^+} = C_{OH^-} + C_{ClO^-} + C_{Cl^-} + C_{GCOO^-} \tag{33}$$

K_b is absolutely unknown, but it is reasonable to assume a value similar to the acetic acid dissociation constant, i.e. 10^{-5} at 20°C.

Polysaccharide oxidation causes the disappearance of sodium hypochlorite and the formation of carboxylic groups on the glucosidic chains. As a result, the pH of the solution decreases rapidly for both the elimination of the alkaline agent NaClO and the formation of acidic carboxylic groups. The decomposition of NaClO contributes to the decrease in pH. The simultaneous integration of eqns (5), (14) and (15) reproduces the decrease in pH for the above-mentioned effects.

By solving eqns (26–33) at any integration step, it is possible to define how much NaClO must be added to keep the pH constant at pH 8 and then to compare this quantity with the experimental data. Kinetic parameters for both decomposition and oxidation have been determined by mathematical regression (Buzzi-Ferraris, 1975) on the experimental results and are given in Table 4. As can be seen, the decomposition parameters obtained in this way are quite similar to those obtained from hypochlorite decomposition runs, i.e. in the absence of the organic substrate, confirming the validity of the approach.

At the end of the NaClO addition, we tested the reliability of the kinetic model by comparing measured and calculated values for the residual chlorine. Then, oxidation and decomposition continued and the described kinetic model was also able to follow the disappearing NaClO in batch conditions.

An example of the agreement obtained in simulating the runs with the parameters reported in Table 4 is given in Fig. 9. The fit obtained is largely satisfactory considering the large number of parameters employed, and their uncertainty, as, for example, in the case of k_a and k_b.

The model allows the determination of all the reagents and products at any instant, as well as of the NaClO consumed by oxidation and decomposition, respectively and the oxidation degree.

In Table 5, the oxidation kinetic constants obtained for different substrates at 20°C are given for comparison purposes. Reactivity differences, assuming 1 for starch, are about 3 for dextrin and 20 for maltotriose. These differences must be ascribed to the greater mobility and availability of small molecules apart from the higher number of easily oxidizable aldehydic terminals in this type of molecule.

In particular, a deep oxidation of the carbohydrates

Table 5. Comparison of the oxidation kinetic parameters obtained for different substrates at 20°C

Substrates	K_o (litres/(mol min))
Starch	$(8{\cdot}1 \pm 0{\cdot}9) \times 10^{-3}$
Dextrin	$(2{\cdot}3 \pm 0{\cdot}3) \times 10^{-2}$
Maltotriose	$(1{\cdot}7 \pm 0{\cdot}2) \times 10^{-1}$

can also give degradation, with the formation of by-products such as oxalic acid.

As NaClO consumption is much faster in the case of small molecules, applying the same reacting ratio (moles of hypochlorite/mole of glucosidic units) we obtain products with a higher oxidation degree in the case of polyglucosides of low molecular weights, corresponding to a higher sequestering power.

CONCLUSIONS

The oxidation of polyglucosides such as starch, dextrins and hydrolized dextrins with sodium hypochlorite gives products that are very active as calcium sequestrants. Unfortunately, oxidized starch and dextrins are poorly biodegradable, while biodegradability strongly increases by decreasing the average molecular weight, as in the case of hydrolized dextrin. Therefore, hydrolized dextrins after oxidation are of potential use as tripolyphosphate substitutes in detergent formulations.

The oxidized carbohydrates obtained by using sodium hypochlorite as oxidant have about the same sequestering properties in respect to the products obtained using sodium periodate and sodium chlorite. This fact suggests that sodium hypochlorite mainly oxidizes carbon atoms in positions 2 and 3 of the glucosidic unit, breaking the corresponding bond and giving two carboxylic groups. The NMR analysis confirms this qualitative observation.

The oxidation reaction rates strongly depend upon pH, molecular weight of the polyglucoside and temperature. pH must be alkaline to avoid hydrolysis and pH = 8 gives a maximum rate, probably corresponding to the maximum HClO concentration in respect to the other possible oxidizing species Cl_2 and ClO^-.

Reactivity of polyglucosides and biodegradability of the corresponding oxidized products both seems to be strictly related to the molecular weights. The reactivity observed for starch, dextrin and hydrolysed dextrins (enzymatic hydrolysis with α-amylase) are about 1/3/20, respectively, probably reflecting the accessibility and susceptibility of oxidizable sites. It must be pointed out, in particular, that decreasing the average molecular weight strongly increases the number of highly oxidizable aldehydic terminals.

As a consequence of the higher reactivity, the oxidation of low molecular weight carbohydrates occurs with higher yields with respect to sodium hypochlorite, because there is less decomposition of this reagent.

In the meantime, the substrate becomes more deeply oxidized (see Table 1) and shows, therefore, a higher sequestering power, in agreement with the observation of Floor *et al.* (1989) that above a critical value of the carboxyl content more effective calcium complexing sites are created. The possibility of producing by-products of low molecular weight as a consequence of a deep oxidation, or on the other hand of having low oxidation yields, clearly indicate the importance of knowing the kinetic behaviour of both oxidation and hypochlorite decomposition.

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