An improved kinetic model for the periodate oxidation of starch

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The kinetics of the periodate oxidation of starch to dialdehyde starch have been studied thoroughly based on a reliable high-performance liquid chromatographic analysis. Investigation of the early stage of reaction has revealed that it proceeds initially following second-order kinetics. Later on, however, the resulting second-order model deviates from the experimental data. In order to get a model for the course of the total reaction, the kinetics have been approached from a different angle. Based on elementary kinetic principles, an appropriate model has been derived that can be used to simulate the oxidation process. An oxidation process performed semi-continuously has been modelled and compared with a batch process.

(Keywords: dialdehyde starch; periodate oxidation; kinetic model)

INTRODUCTION

Glycol cleavage oxidation is a useful tool in carbohydrate chemistry to produce dialdehyde compounds. The Malaprade reaction with periodate is known as a selective procedure in oxidative diol-scission reactions. However, owing to the price of the oxidant, stoichiometric reactions with periodate are not favourable for industrial purposes. Therefore, regeneration of periodate has been investigated electrochemically[1–4]. In the 1960s these electrochemical regeneration processes were combined with the oxidation of starch to dialdehyde starch[5–20]. Various applications for this functionalized polymer have been reviewed[15–21]. An economically feasible process, however, has not been found up to now.

In previous studies, the current efficiency of electrochemical devices has been the main topic of interest. Reinvestigation of periodate regeneration reveals that a low dissipation of periodate, e.g. by contamination with metal from the electrodes, impurities, or inefficient washing of the product, results in a tremendous effect on the costs. These problems can be solved by applying a catalytic amount of periodate, continuously regenerated in a separate cell. In order to realize an efficient combination of oxidation and regeneration, kinetic data of both reactions have to be available.

Parameters describing the kinetics of amylose oxidation with periodate have been published[22–26]. The degree of oxidation is indirectly determined by measuring periodate consumption during the reaction by iodometric titration[22–26]. However, this titration is hindered because of an interfering complexation of iodine with amylose. A decline of the second-order rate constant is attributed to inter-residual hemi-acetal formation between aldehyde groups and unoxidized diol systems[23–26].

In the present study, the kinetics of the periodate oxidation of starch have been studied using a more reliable method, namely high-performance liquid chromatographic (h.p.l.c.) analysis. A model describing the oxidation is proposed, based on the experimental data obtained at both an initial time interval and during the course of reaction.

The readily available aldehyde functions in dialdehyde starch have been determined by the reaction with hydroxylamine hydrochloride to oximes.

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EXPERIMENTAL

Materials

Potato starch was supplied by Avebe and pure sodium metaperiodate by Merck. The 0.1 M sodium hydroxide eluant for the h.p.l.c. analysis was derived from a 50% sodium hydroxide solution Baker analysed and milliQ-water. All other reagents were analytical-grade commercial products.

Reactor

Oxidation on preparative scale was performed in a 500 ml thermostatted glass reaction vessel. During the reaction, the pH was controlled using a pH meter (Metrohm 654), a pH controller (Metrohm 614) and a motor burette (Metrohm 665, 10 ml) containing 0.1 M aqueous sodium hydroxide.

Oxidation procedure

General preparation method of (partially) periodate-oxidized starch. To a suspension of potato starch in 300 ml water was added an amount of periodate, in varying molar concentrations. The initial pH was adjusted (pH 3–5) and kept constant during reaction. Various batches of (partially) dialdehyde starch were prepared under several conditions (*Table 1*). All reactions (1a–1d, 2a–2c) were allowed to proceed at 25°C.

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Table 1 Conditions for preparation of periodate-oxidized potato starch: initial concentration of glucose (g) and of periodate (p), pH and total reaction time. The degree of oxidation x/g is determined after h.p.l.c. analysis

Batch no.	g (M)	p (M)	p/g	pH	Time (h)	x/g
1a	0.41	0.163	0.4	5.0	1.5	0.395
1b	0.41	0.206	0.5	5.0	1.5	0.500
1c	0.41	0.246	0.6	5.0	1.5	0.593
1d	0.41	0.49	1.2	5.0	48	0.97
2a	0.19	0.19	1	5.0	1.0	0.54
2b	0.19	0.19	1	4.0	1.0	0.58
2c	0.19	0.19	1	3.4	1.0	0.57

Determination of reaction rate on granular potato starch. Periodate solution (1 ml) of an appropriate concentration was added to 1–25 mg potato starch in a gas chromatography (g.c.) sample vial of 2.5 ml. The reaction mixtures (pH 5) were kept in the dark and stirred at 25°C for different reaction times (30 s to 8 h). The reactions were quenched by addition of a 0.6 M aqueous solution of sodium borohydride in 0.1 M sodium hydroxide to reduce the periodate. Reproducible sampling was impossible owing to the inhomogeneity of the reaction mixture. Hence, separate reactions were necessary for each reaction time, and several series of experiments were required, dealing with various initial concentrations of the reactants. These series can be divided into three groups with respectively an excess starch (3a–3c), an excess periodate (4a–4b) and both reactants applied stoichiometrically (5a–5c) (*Table 2*). Every reaction mixture was analysed by h.p.l.c.

Determination of reaction rate on gelatinized potato starch. A suspension of 4.92 g starch (dry weight) in 200 ml water was gelatinized at 90°C for 10 min in a glass vessel under temperature-controlled conditions. The stoichiometric amount of periodate (6.42 g) dissolved in 100 ml water was added immediately after cooling to 25°C. The initial concentration of periodate and starch thus obtained was 101 mM (*Table 2*). At small time intervals 1 ml samples were quenched with sodium borohydride and further prepared for h.p.l.c. analysis or analysed by iodometric titration.

Isolation procedure

The reaction slurries were filtered on a Buchner filter (Whatman 54 filter paper), and washed several times with water to remove all (reduced) periodate. The presence of iodate and periodate in the wash water was indicated as iodine after addition of excess potassium iodide and hydrochloric acid. The washed products were freeze-dried.

H.p.l.c. apparatus

The analyses were performed on a Dionex DX 300 h.p.l.c. unit, equipped with an advanced gradient pump module (0.1–10 ml min^{-1}), a pulsed electrochemical detector, an SP 8880 autosampler and a 4 × 250 mm CarboPac MA1 column.

Analysis procedure

Iodometric titration. Samples (1 g) were withdrawn at small time intervals from a homogeneous reaction mixture of gelatinized starch and pipetted into 10 ml of a solution of 0.5 M phosphate bufier (pH 7) and 0.18 mM potassium iodide. The liberated iodine was titrated with 0.01 M sodium thiosulfate, with starch as the indicator[26].

Table 2 Initial concentrations of starch (g) and periodate (p) applied in series to determine the reaction rate of granular (3a–5c) and gelatinized starch (6) at 25°C

Series no.	g (mM)	p (mM)
3a	123	12.4
3b	123	24.8
3c	123	37.0
4a	4.94	47.2
4b	11.1	47.2
5a	61.7	61.7
5b	123	123
5c	185	185
6	101	101

H.p.l.c. analysis. Prior to analysis the (partially) oxidized starch was reduced either in the crude reaction mixture (1–25 mg ml^{-1}) or after isolation (25 mg), by adding 1 ml of an aqueous solution of sodium borohydride (0.8 M) and sodium hydroxide (0.1 M). The reduction was allowed to proceed for 24 h at 25°C, while stirring. To this medium, 1 ml of an aqueous mannitol solution (1–25 mg ml^{-1}) was added as internal standard. Subsequently, the polyalcohol was hydrolysed by adding 60 μl sulfuric acid and stirring at 95°C, for 10 h. The resulting sample was diluted to a final concentration of 10 $\mu g\ ml^{-1}$ and subsequently injected onto the h.p.l.c. column, with an eluant flow (0.1 M NaOH) of 0.4 ml min^{-1}.

Oxime formation. To a suspension of 500 mg dialdehyde or partially oxidized starch in 30 ml water at 25°C and pH 5 was added 4 ml aqueous hydroxylamine hydrochloride (1 M, pH 5). The pH was kept constant automatically using a pH meter (Metrohm 654), a pH controller (Metrohm 614) and a motor burette (Metrohm 665, 10 ml) with 1 M aqueous sodium hydroxide. The amount of sodium hydroxide consumed was measured until completion of reaction.

RESULTS AND DISCUSSION

The oxidation of potato starch with periodate results in the production of dialdehyde starch and some traces of formic acid. The formic acid is liberated after oxidation of the end-groups of the polymer chain or new introduced end-groups after hydrolysis of glycosidic bonds.

Investigation of the periodate consumption by iodometric titration gave no reliable data, owing to complexation of iodine with amylose. This has been

observed as an overconsumption of thiosulfate to reach the end-point and a remaining blue colour of the granules.

H.p.l.c. analysis has been performed after reduction and hydrolysis of the reaction mixtures. Partially oxidized starch is mainly converted to erythritol and glucose, and some traces of sorbitol[27]. Erythritol and glucose, resulting from respectively oxidized and non-oxidized anhydroglucose units, have been determined quantitatively in a reproducible way. Repeated analyses of the reaction mixture revealed the relative standard deviation of the results to be lower than 2%. The amount of sorbitol, resulting from unoxidized end-groups, was found to be constant during the total reaction time. The absence of degradation was evidenced by a constant sum of erythritol and glucose during the whole period and negligible formation of formic acid. As no negative side reactions have been observed, the measured quantity of erythritol was related to the amount of periodate consumed. The degree of oxidation can be expressed as the molar ratio of erythritol to the total amount of starting material.

The reactions to prepare dialdehyde starches with a degree of oxidation of 60% and lower (1a–1c) were completed within 90 min. The calculated degree of oxidation corresponded considerably well with the applied molar ratio of periodate to starch. Complete oxidation (1 d) was very difficult to achieve even after 2 days of reaction with excess periodate (*Table 1*).

The influence of pH on the reaction rate has been investigated in separate series of reactions (2a–2c). A decrease of the pH to 3.4 had no negative effect on the degree of oxidation after 1 h of reaction (*Table 1*).

Symbols

The following symbols are used in this work:

g = initial starch concentration expressed as total initial concentration of anhydroglucose units
p = initial periodate concentration
x = erythritol concentration at any time t; $x = 0$ at $t = 0$
G = concentration of unoxidized anhydroglucose units in oxidized starch at any time t ($G = g - x$)
P = periodate concentration at any time t ($P = p - x$)
x/g = degree of oxidation
μ = 1 − degree of oxidation ($\mu = 1 - x/g$)

Determination of reaction order at t = 0

The oxidation of native potato starch with sodium periodate is followed during the first 5 min of reaction. It can be assumed that complications caused by the presence of secondary reactions do not occur within this short time interval. The order of starch and periodate in the rate equation is studied by performing the oxidation with a large excess of either starch or periodate (3a–3c and 4a–4b respectively). The amount of erythritol liberated as a function of time is depicted in *Figure 1* and the rate at $t = 0$ (v_0) is determined by the slope of the resulting straight line (*Table 3*).

Table 3 Initial reaction rate v_0 in series 3a–4b

Series no.	3a	3b	3c	4a	4b
v_0 (10^{-6} M s^{-1})	11.0	24.8	40.7	2.43	5.30

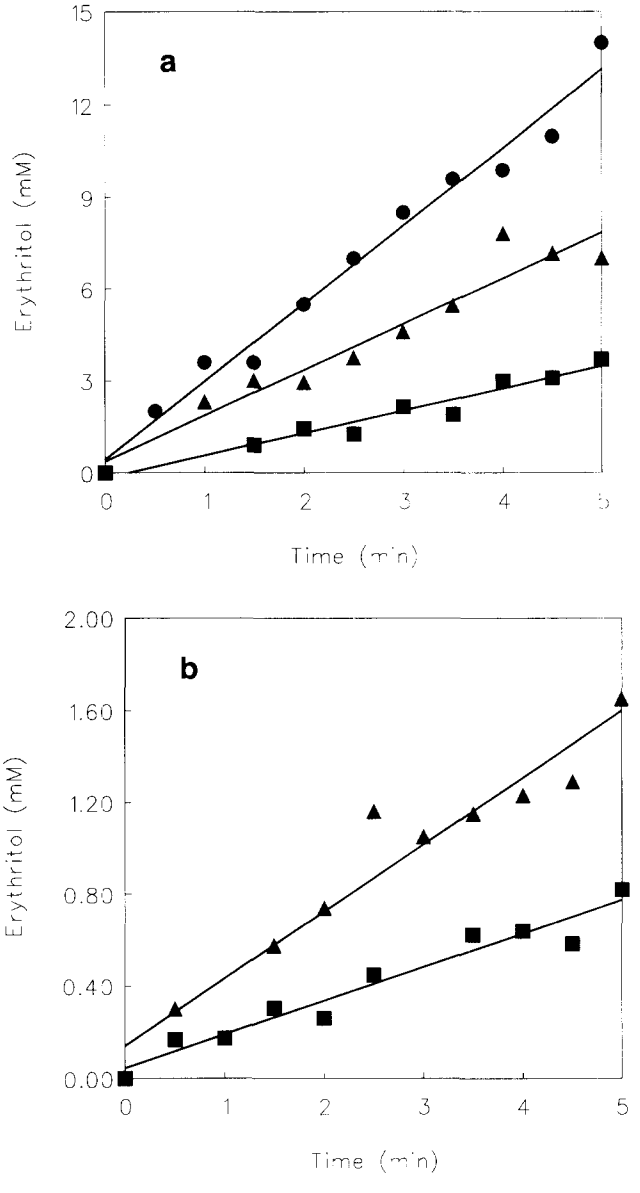


Figure 1 Amount of erythritol liberated during the first 5 min of reaction as determined by h.p.l.c. in series 3a–3c and 4a–4b. (a) With excess starch (g = 123 mM): (■) p = 12.4 mM; (▲) p = 24.8 mM; (●) p = 37.0 mM. (b) With excess periodate (p = 47.2 mM): (■) g = 4.94 mM; (▲) g = 11.1 mM

The logarithm of the initial rate is a linear function of the logarithm of the initial concentration of either reactant, with a slope equal to one. Consequently, the periodate oxidation of starch may be considered to follow second-order kinetics during the initial phase of reaction.

Determination of the rate constant k *at* t = 0

According to second-order kinetics the reaction can be described by the following equation:

$$\ln\left(\frac{g-x}{p-x}\right) = -\ln\left(\frac{p}{g}\right) + k(g-p)t \qquad (1)$$

The rate constant k is derived from the experimental data in *Figure 1* by determination of the slope of the function $\ln[(g-x)/(p-x)]$ vs. time. These values are summarized in *Table 4*, together with the calculated $-\ln(p/g)$ and graphically derived intercept. The close fit between

Table 4 Intercept and k values at $t = 0$ calculated with equation (1) for series 3a–4b

Series no.	$-\ln(p/g)$	Intercept	k ($M^{-1} s^{-1}$)
3a	2.29	2.28	0.009
3b	1.60	1.60	0.010
3c	1.20	1.21	0.012
4a	−2.26	−2.23	0.012
4b	−1.45	−1.45	0.011

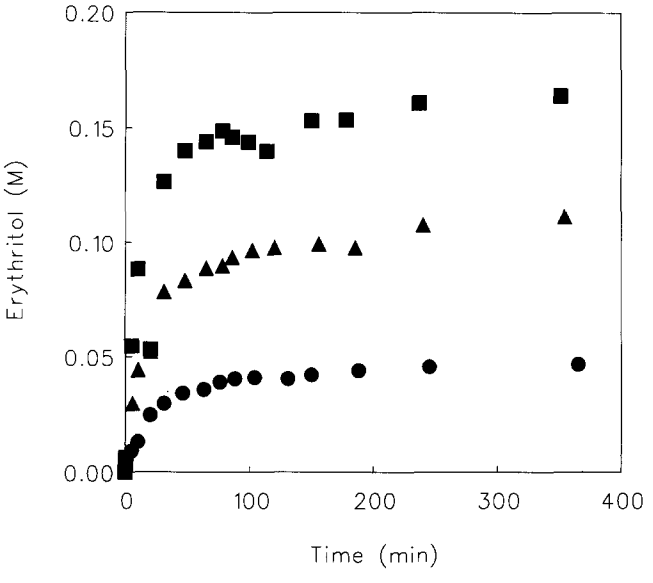


Figure 2 Erythritol (x) determined with h.p.l.c. *versus* time in series 5a–5c. Initial concentrations of periodate and starch: (●) 61.7 mM; (▲) 123 mM; (■) 185 mM

the last-mentioned values corroborate the resulting average k constant of 0.011 ± 0.001 $M^{-1} s^{-1}$ (*Table 4*).

Course of reaction

In series 5a–5c and 6, the oxidation of potato starch is followed with a stoichiometric amount of sodium periodate for several hours. The course of erythritol formation during the reaction is given in *Figure 2*. The data appear to deviate from second-order kinetics after an initial period of 5 to 10 min. Consequently, in spite of previous results, an appropriate second-order model cannot be proposed. It is observed that the oxidation proceeds quickly until a degree of oxidation of about 50%, usually at 30 min of reaction, is reached. From this moment the rate starts to decline considerably.

The course of reaction is alternatively described by considering the starch molecule as a polymer consisting of a fixed amount of monomers, either oxidized or unoxidized. It is assumed that the rate of reaction is determined by (i) the collision between a unit in the (partially oxidized) starch molecule and a periodate molecule ($P_1 = g(p - x)$) and (ii) the probability of attack of an unoxidized unit ($P_2 = \mu = (g - x)/g$). In partially oxidized starch two different types of unoxidized units with different reactivities k_1 and k_2 need to be distinguished: (i) those without an inhibiting effect of neighbouring aldehyde groups ($P'_3 = \mu$) and (ii) those protected by hemi-acetal or acetal formation ($P''_3 = 1 - \mu$). It is assumed that only one neighbour of an oxidized unit is protected from periodate action[24–26].

Table 5 The k_1 values calculated with equation (8) for series 5a–6

Series no.	5a	5b	5c	6
k_1 ($M^{-1} s^{-1}$)	0.013	0.013	0.010	0.014

Based on previous considerations, the following rate equations are derived, for free and inhibited anhydroglucose units respectively:

$$\frac{dx}{dt} = k_1 \mu^2 g(p - x) \tag{2}$$

$$\frac{dx}{dt} = k_2 \mu(1 - \mu) g(p - x) \tag{3}$$

Combination of equations (2) and (3) results in the general rate equation:

$$\frac{dx}{dt} = \mu[k_1 \mu + k_2(1 - \mu)] g(p - x) \tag{4}$$

Rearrangement of this equation and substitution of μ gives the next differential, as a general model for the periodate oxidation of the starch polymer:

$$\frac{dx}{dt} = \frac{1}{g}[k_1(g - x) + k_2 x](g - x)(p - x) \tag{5}$$

If k_1 and k_2 are equal, a second-order equation would result, which is in contrast with the experimental observations. Fitting of the experimental data with equation (5) revealed k_2 to be much smaller than k_1. Consequently, the previous formula can be simplified as:

$$\frac{dx}{dt} = \frac{k_1}{g}(g - x)^2(p - x) \quad k_2 \ll k_1 \tag{6}$$

Under stoichiometric conditions ($g = p$, $G = P$), the following equation arises:

$$\frac{dx}{dt} = \frac{k_1}{g}(g - x)^3 \quad g = p \tag{7}$$

Integration results in a function that enables calculation of the concentration of unoxidized anhydroglucose units G at any time t under the applied conditions (pH 5, 25°C):

$$G = \frac{g}{(1 + 2k_1 gt)^{1/2}} \quad g = p \tag{8}$$

The experimental h.p.l.c. data of oxidation on granular and gelatinized starch can be fitted with the non-linear regression analysis program NONLIN, using equation (8) (*Figure 3*). The k_1 values (*Table 5*) derived from these fits are in close agreement with the earlier determined initial rate constant k. Moreover, no significant difference is observed between the rate constants of granular and gelatinized starch. This implies that the physical state of the starch is of minor importance in this respect.

Modelling

With the equations thus obtained, the course of the oxidation and the corresponding reaction time can be predicted in several different systems:

(i) a batch process performed stoichiometrically ($p = g$; equations (7) and (8));

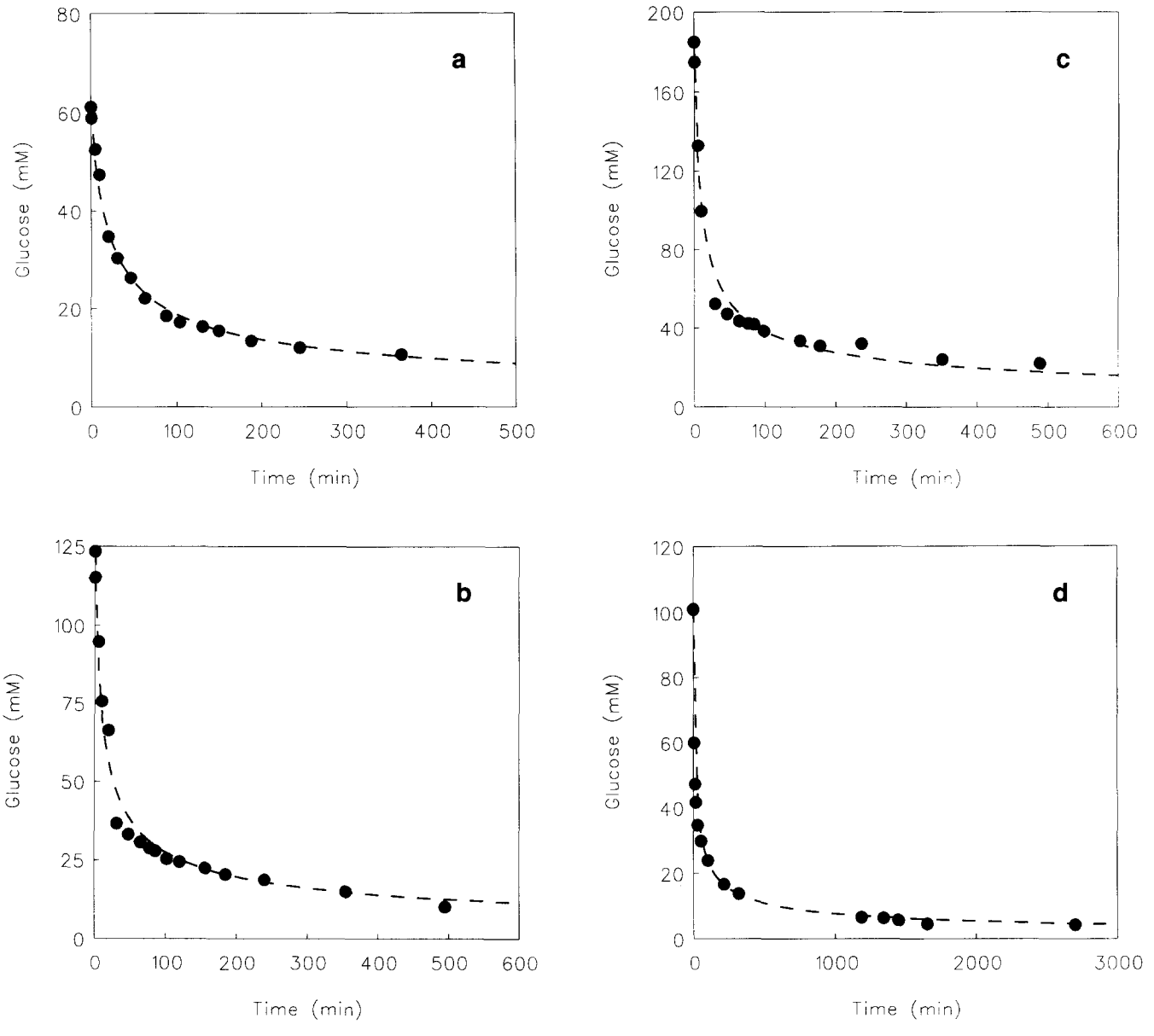


Figure 3 Fit of experimental data of series 5a–5c and 6 with equation (8). Initial concentrations of periodate and starch: (a) 61.7 mM, granular starch; (b) 123 mM, granular starch; (c) 185 mM, granular starch; (d) 101 mM, gelatinized starch

(ii) a non-stoichiometric batch process to produce partially oxidized starch ($p = ag$) with $0 < a \leqslant 1$ in equation (6); and

(iii) a semi-continuous process in which the reduced periodate will be continuously cycled through the cell with immediate regeneration in a separate electrochemical device, in order to keep the periodate concentration constant.

In the latter case ($P = p =$ constant), equation (6) can be simplified as:

$$\frac{dx}{dt} = \frac{k_1}{g}(g - x)^2 p \quad P = p = \text{constant} \qquad (9)$$

After integration of equation (9) the following relation arises:

$$G = \frac{g}{1 + k_1 pt} \quad P = p = \text{constant} \qquad (10)$$

In *Figures 4a–4d* some models of semi-continuously performed processes are compared with a batch process. With respect to the batch process the chosen ratio of periodate to starch was equal to the desired degree of oxidation at completion of reaction. In a semi-continuous process, every degree of oxidation can be yielded, even at very low concentration ratios, depending on the desired reaction time. The minimal ratio of periodate to starch to be applied in a semi-continuous process in order to realize a comparable performance as in a batch process depends on the desired degree of oxidation and the initial concentration of starch. Even at a ratio of 2–5% on a molar basis, the rate of a semi-continuous oxidation can be equivalent to that of a batch process. A fast reaction, obtained at the higher ratios of periodate to starch, has to be weighed against the advantages of a small concentration of periodate compared to starch. Essentially, a small periodate concentration will enable the losses of this expensive oxidant to be minimized considerably.

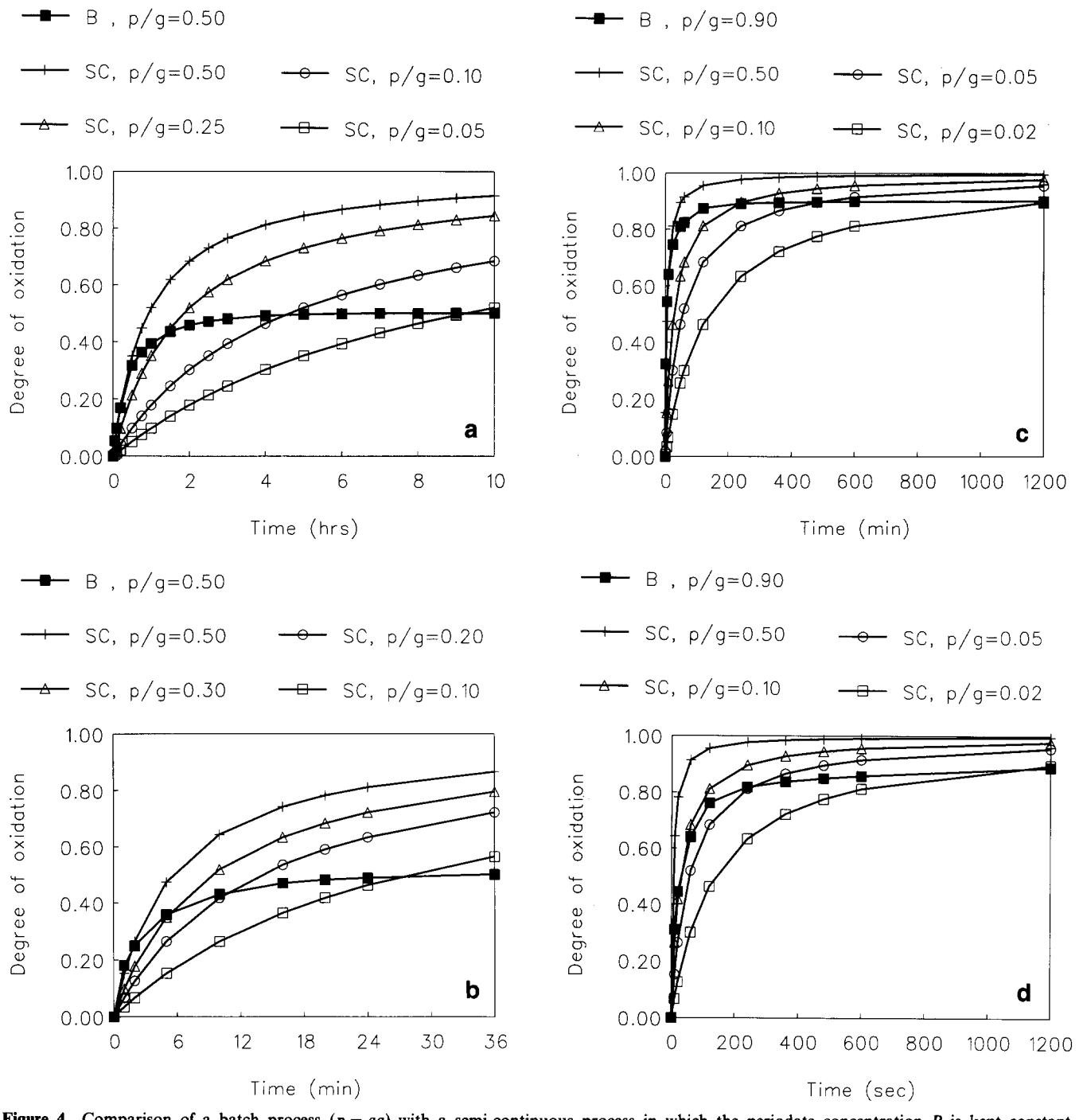


Figure 4 Comparison of a batch process ($p = ag$) with a semi-continuous process in which the periodate concentration P is kept constant through regeneration ($P = p$ = constant), for different ratios of periodate to starch. Initial concentrations of starch: (a) 0.06 M; (b) 0.6 M; (c) 0.6 M; (d) 6 M

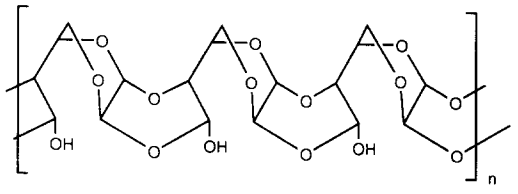
Oxime formation

The protection of the alcohol functions towards oxidation is evidenced by testing the ability of the aldehyde groups to form oximes during treatment with hydroxylamine hydrochloride. The moles of oxime groups per anhydroglucose unit are calculated from the amount of hydrochloric acid titrated with sodium hydroxide[28]. In *Table 6* the results are compared with the degree of oxidation determined by h.p.l.c. analysis. In partially oxidized starch only 52 to 54% of the expected aldehyde functions are immediately available for this reaction. Completely oxidized starch has a somewhat higher percentage of free aldehyde functions (66%). The addition of native starch to the suspension had no influence on the previous observations.

Table 6 Fraction of reacted aldehyde groups after treatment with hydroxylamine hydrochloride in comparison with the degree of oxidation x/g of the dialdehyde starch

Batch no.	x/g	Oxime (g)	CHO reacted (%)
1a	0.395	0.410	52
1b	0.500	0.540	54
1c	0.593	0.640	54
1d	0.97	1.280	66
1d + native	0.97	1.282	66

In dialdehyde starch each aldehyde group can be hydrated and form cyclic hemi-acetals with alcohol groups present in the neighbourhood. The most probable combinations are (i) intra-unit, C2–C6 and



Scheme 1 Hemi-acetal and acetal formation in dialdehyde starch

C2–C3, and (ii) inter-unit, C2–C3′ and C3–C2″. It can be assumed that the difference in reactivity of all these possible hemi-acetal functions is negligible, which is in contrast with our experimental observations. Hence, we propose the formation of an acetal on C2 with C6 and C3′, and a hemi-acetal at C3 with C2″ (*Scheme 1*). The reactivity of the acetal will be less compared with the hemi-acetal, which confirms the inhibition of one adjacent diol unit towards oxidation.

CONCLUSION

A reliable h.p.l.c. method is applied to investigate the kinetics of the diol-scission reaction of glucose moieties in starch to dialdehydes. After reduction and hydrolysis of the dialdehyde starch, the liberated glucose and erythritol can be determined quantitatively. The degree of oxidation can be followed accurately in time.

The reaction is described at $t = 0$ with a second-order rate equation. Owing to inhibition by hemi-acetal structures, the experimental data deviate distinctly from this model, after 5–10 min.

The approach in which starch is considered as a polymer, instead of a certain amount of free glucose moieties, enables the development of a model convenient to the experimental data. A general model is derived to describe the course of the total reaction. A supplementary rate constant has been introduced to characterize the reaction of protected diol units. The latter reaction only occurs significantly after 50% oxidation.

A protection of the aldehyde groups towards reaction is demonstrated. The underlying effect is a hemi-acetal forming reaction with neighbouring alcohol groups.

According to the description of the reaction presented here, a semi-continuous process with separate oxidation and regeneration will require the shortest reaction times. Even a small ratio of periodate to starch, a condition that will be favourable in an industrial process, yields high performances.

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