The kinetics of the homogeneous benzylation of potato starch in aqueous solutions

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Received 22 May 2002; accepted 25 May 2002

Abstract

The reaction rates in the base-catalysed benzylation of gelatinized aqueous starch (4 wt%), by benzyl chloride (BzCl), were investigated in a semibatch reactor at temperatures ranging from 50 to 80°C. The desired starch benzylation reaction is accompanied by an undesired parallel base-catalysed hydrolysis reaction of benzyl chloride. The rate equations are:

- Starch benzylation: \( R_{\text{BzCl}} = k_2 c_{\text{RO}} c_{\text{BzCl}} \)
- Benzyl chloride hydrolysis: \( R_{\text{BzCl}} = k_3 c_{\text{OH}} c_{\text{BzCl}} \)
- Neutral benzyl chloride hydrolysis: \( R_{\text{BzCl}} = k_4 c_{\text{H}_2\text{O}} c_{\text{BzCl}} \)

where \( c_{\text{BzCl}} \) is the benzyl chloride concentration, \( c_{\text{RO}} \) is the concentration of the dissociated starch hydroxyl group and \( c_{\text{OH}} \) is the sodium hydroxide concentration; \( k \) is the reaction rate constant. The temperature dependency of the rate constants was measured as:

- \( k_2 = 4.21 \times 10^{11} \cdot e^{-86.2 \times 10^3 / RT} \)
- \( k_3 = 2.62 \times 10^8 \cdot e^{-85.5 \times 10^3 / RT} \)
- \( k_4 = 9.72 \times 10^9 \cdot e^{-76.9 \times 10^3 / RT} \)

where \( R = 8.31441 \text{ J/(mol K)} \).

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Keywords: Kinetics; Benzylation; Modified starches; Homogeneous; Potato starch

1. Introduction

Modified starches are used in numerous applications and industrial processes (de Graaf, Broekroelofs, Janssen, & Beenackers, 1995). One of these applications is the use of benzylated starch as paper finisher (Wurtzburg, 1986). In general, suspension processes are used for the production of this starch derivative. The disadvantage of this process is that both temperature and hydroxide concentrations have to be kept low, in order to prevent gelatinization and thus mixing problems. Low reaction rates and selectivities are the result. An alternative to this problem is the use of reactive extrusion (de Graaf & Janssen, 2000; de Graaf, Broekroelofs, & Janssen, 1998). This reactor is very suitable in handling high viscous solutions, thus higher temperatures, selectivities and conversions are the result. Still, before a reactive extrusion process can be developed the kinetics of the benzylation reaction should be known. Earlier workers have described a number of methods for the preparation of this ether (Asahina & Nara, 1934; Gomberg & Buchler, 1921; Makarov & Andrianov, 1933a,b, 1934, 1935, 1936) but no kinetic data were presented. In case of the heterogeneous reaction only Homan Free, Joosten, Roelfsema, and Stamhuis (1985) have determined the kinetics of potato starch benzylation in an aqueous starch suspension. To our knowledge no information on the homogeneous kinetics has been published. We therefore have investigated the kinetics of starch benzylation in a homogeneous solutions under alkaline conditions.

Starch granules consist of polymers of \( \alpha \)-D-glucose, with minor lipid and protein components. The polymers consist...
of linear poly-(1→4)-α-D-glucan amylose and branched amylopectin, where linear (1→4)-α-D-glucan chains are connected through (1→6)-α linkages. In the case of etherification, the hydrogen atoms of starch hydroxyl groups are substituted by other functional groups. For benzylation, the reaction scheme is as follows:

\[
\text{ROH} + \text{BzCl} \xrightarrow{k_1} \text{ROBz} + \text{HCl}
\]

(a)

\[
\text{RO}^- + \text{BzCl} \xrightarrow{k_2} \text{ROBz} + \text{Cl}^-
\]

(b)

\[
\text{H}_2\text{O} + \text{BzCl} \xrightarrow{k_3} \text{BzOH} + \text{HCl}
\]

(c)

\[
\text{OH}^- + \text{BzCl} \xrightarrow{k_4} \text{BzOH} + \text{Cl}^-
\]

(d)

\[
\text{OH}^- + \text{HCl} \xrightarrow{k_5} \text{H}_2\text{O} + \text{Cl}^-
\]

(e)

Here, ROH represents the hydroxyl groups of the starch molecule, RO\(^-\), the nucleophilic strach groups, OH\(^-\), the hydroxide ions, BzCl, benzyl chloride (C\(_6\)H\(_5\)CH\(_2\)Cl), BzOH, benzyl alcohol (C\(_6\)H\(_5\)CH\(_2\)OH) and starch benzyl ether is represented by ROBz.

The average number of substituent per D-glucose unit is given by the degree of substitution, which is abbreviated as DS. A DS of 1.0 means that an average of one substituent per D-glucose unit is present. Each D-glucose unit possesses three reactive hydroxyl groups so the maximum possible DS is 3. The nucleophilic groups of the starch molecule (RO\(^-\)) are formed through the abstraction of a proton from one of the three hydroxyl groups by a hydroxide ion, according to:

\[
\text{OH}^- + \text{H}_2\text{O} \xrightarrow{k} \text{RO}^- + \text{H}_2\text{O}
\]

(f)

The weakly acidic character of the hydroxyl groups has been established by Doppert and Staverman (1966) and de Graaf et al. (1995). Moser (1987) reports that at least one of the three starch hydroxyl groups is a stronger acid than water. In general, acid–base neutralization reactions are instantaneous, (Homan Free et al., 1985) which means that in this case the reaction is always at its equilibrium.

From the equations above, it is noticed that direct consumption of sodium hydroxide takes place via reaction (d) and that the reactions (a) and (c) consume sodium hydroxide indirectly through reaction (e). Less obvious is the indirect consumption of hydroxide ions due to reaction (b), but from reaction (f) it follows that removal of an RO\(^-\) species by reaction (b) will lead to a shift in the equilibrium composition of reaction (f), resulting in the consumption of sodium hydroxide. Each of the four reactions (a)–(d) consumes benzyl chloride.

The benzylation of starch is a nucleophilic substitution reaction. Two widely accepted mechanisms for this kind of reactions are the unimolecular (SN1) and the bimolecular (SN2) reaction mechanism (Solomons, 1976). In the SN1 mechanism, the substrate solvolysis is the rate determining step and the reaction rate is dependent on the substrate concentration only. In the SN2 mechanism, the substrate and the nucleophile react directly via a transition state to form the product. In this case, the rate is dependent on the concentration of both the substrate and the nucleophile.

In general, benzyl chloride reacts with a hydroxyl group either by a SN1 or a SN2 mechanism. As shown below, both the benzylation of starch and the competitive reactions of benzyl chloride with water and hydroxide follow the SN2 mechanism. Using this information, we propose the following kinetic scheme which is an extension of the kinetic equation proposed by Homan Free et al. (1985) for the heterogeneous benzylation:

\[
-R_{\text{BzCl}} = \frac{d[R\text{BzCl}]}{dt} = k_1 c_{\text{ROH}} + k_2 c_{\text{RO}^-} + k_3 c_{\text{H}_2\text{O}} + k_4 c_{\text{OH}^-}
\]

(1)

Here the four terms of the right-hand side of Eq. (1) originate from reactions (a) to (d). Benzyl chloride has a very low solubility in water and the solubility of water in benzyl chloride is negligible, so if this reagent is added in excess to the aqueous starch solution, two phases will be formed: an organic phase consisting of benzyl chloride only and an aqueous phase consisting of the starch solution and dissolved benzyl chloride and sodium hydroxide. If efficient mixing is applied, the aqueous starch phase can be saturated with benzyl chloride throughout the reaction. Therefore, benzyl chloride concentration is constant and equal to its solubility \(c_{\text{BzCl}}\) in water.

Our conclusion is that the neutral hydrolysis of benzyl chloride (reaction (c)) is an SN2 reaction, is in agreement...
with the results presented by Beste and Hammett (1940), Golinkin and Hyne (1968), Robertson and Scott (1961), Ohnishi and Tanabe (1971), and Tanabe and Sano (1962).

The work of Beste and Hammett (1940), Olivier (1934), Olivier and Weber (1934), and Swain and Scott (1953) support the SN2 mechanism for reaction (d). The dissociation of starch is controlled by the equilibrium constant:

\[ K = \frac{c_{RO2}}{c_{ROH}c_{OH2}} \quad (2) \]

Due to the fact that the equilibrium of reaction (f) is established instantaneously, one can express the concentration of RO2 in the concentration of starch, water and hydroxide using Eq. (2):

\[ c_{RO2} = \frac{c_{ROH}c_{OH2}}{c_{H2O}} K \quad (3) \]

Substitution of Eq. (3) in Eq. (1) gives:

\[ R_{BzCl} = k_1'c_{ROH} + k_3'c_{H2O} + \left( \frac{c_{ROH}}{c_{H2O}} k_2' + k_4' \right) c_{OH2} \quad (4) \]

Water and starch are present in excess so that their concentration can be assumed as constant throughout the reaction. Therefore, Eq. (4) can be rewritten as:

\[ R_{BzCl} = k_1' + k_3' + (k_2' + k_4')c_{OH2} \quad (5) \]

with:

\[ k_1' = k_1 c_{ROH} c_{BzCl}; \quad k_3' = k_2 c_{BzCl}; \quad k_3'' = k_3 c_{H2O} c_{BzCl}; \]
\[ k_4' = k_4 c_{BzCl}; \quad k_4'' = k_4 c_{H2O} \quad (6) \]

From Eq. (e), it follows that a plot of the measured rate of benzyl chloride consumption \(-R_{BzCl}\) against the hydroxide concentration for any constant reaction temperature, will yield a straight line with a slope equal to \((k_2' + k_4')\) and an intercept with the vertical axis equal to \((k_1' + k_3')\).

If starch is absent from the reaction system, then only the hydrolysis of benzyl chloride occurs, and Eq. (5) reduces to:

\[ R_{BzCl} = k_3'' + k_4'c_{OH2} \quad (7) \]

Then a plot of the benzyl chloride consumption rate as a function of the hydroxide concentration will yield a line with a slope equal to \(k_3''\) and an intercept equal to \(k_3''\).

The rate of hydroxide consumption in reactions (a), (c), and (d) is equal to the rate of benzyl chloride consumption in these reactions. The same conclusion holds for reaction (b), since equilibrium reaction (f) is instantaneous and both \(c_{ROH}\) and \(c_{H2O}\) remain constant. So the rate of benzyl chloride consumption can be determined by measuring the rate of hydroxide consumption in the reaction mixture.

### 2. Experimental

#### 2.1. Materials

Benzyl chloride (BzCl) and sodium hydroxide were pro analysis grade products of Merck, West Germany. The potato starch was a commercial grade product of AVEBE B.A Cooperatieve Verkoop en Productie van Aardappelmeel en Derivaten, the Netherlands.

#### 2.2. Equipment and procedures

First measurements, with a system consisting of water, sodium hydroxide and benzyl chloride were performed for the determination of the benzyl chloride hydrolysis kinetics (reactions (c) and (d)). Secondly, starch benzylation experiments were carried out in a system containing an aqueous solution of sodium hydroxide and approximately 6% starch in equilibrium with benzyl chloride as the second liquid phase.

A simplified diagram of the equipment used is given in Fig. 1. All the experiments were carried out in double walled vessels, which were thermostatet. In each vessel, the pH-value (pH electrode from Amagrus Elektroden Gmbh, Germany) and the temperature (PT-100 thermocouples) was measured. The signals were send to a computer for subsequent processing. All the experiments were conducted at a constant pH which was maintained by continuous hydroxide addition.

### 3. Results and discussion

#### 3.1. Hydrolysis of benzyl chloride

As mentioned above, a constant pH is maintained because the consumed hydroxide and benzyl chloride...
amounts are equal to the added hydroxide amount. Fig. 2 shows a typical result of the added hydroxide solution amount as a function of time. Two regimes can be distinguished:

I Initially, the reaction phase remains saturated with benzyl chloride and because the hydroxide concentration is kept constant, this results in a constant reaction rate. Indeed this is observed experimentally from the constant slope of the graph in this region.

II Finally, the benzyl chloride amount in the system has been reduced to such a level that saturation of the reaction phase is no longer possible. The concentration of benzyl chloride decreases while the reaction rate reduces and ultimately approaches zero.

The linear part of the graph is used for the calculation of kinetic parameters. The reaction rate was calculated from:

\[ -R_{\text{BzCl}} = \frac{\dot{F}_{\text{OH}} N}{V_r} \]  

(8)

here \( \dot{F}_{\text{OH}} \) is the rate at which the hydroxide solution is added to the reactor, given by the slope of the left part of the curve in Fig. 2 (m³/s), \( N \), the concentration of the hydroxide solution fed to the system (kmol/m³) and \( V_r \), the volume of the reaction phase (m³).

The results of the hydrolysis experiments are given in Table 1 and Fig. 3. The kinetic rate expression for hydrolysis is given by Eq. (9).

\[ -R_{\text{BzCl}} = k_3^b + k_4^b \dot{c}_{\text{OH}}^b \]  

(9)

From Fig. 3, the constants \( k_3^b \) and \( k_4^b \) can be calculated from the slopes and intercepts, respectively. The results are summarized in Table 2.

In order to calculate the reaction rate constants \( k_3 \) and \( k_4 \), the solubility of benzyl chloride in water is needed. Due to the fact that benzyl chloride hydrolyses readily at the relevant reaction temperatures, only limited information is available of its solubility in water. In this work, the solubility was determined by a method similar to that of Ohnishi and Tanabe (1971). Their method can be summarized as follows: first an excess amount of benzyl chloride is added to water at a specific temperature. One phase, of the obtained two-phase system, consists entirely of benzyl chloride. The second phase consists of water saturated with benzyl chloride (\( c_{\text{BzCl,s}} \)). The neutral hydrolysis rate (\( V \), according to their notation) was measured under these conditions. Secondly, the hydrolysis rate, \( V \), is measured at various benzyl-chloride concentrations below its solubility in water. According to their findings, the next kinetic equation holds for the neutral hydrolysis of benzyl chloride at low temperatures:

\[ V = k_5^p c_{\text{BzCl}} + k_6^p c_{\text{BzCl}}^2 \]

The contribution of the second term to the total reaction rate decreases rapidly with increasing temperature, having the values 36.9, 32.6 and 9.25% at 4.5, 20 and 30 °C.

### Table 1

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( c_{\text{OH}} \times 10^{-3} ) (kmol/m³)</th>
<th>( \dot{F}_{\text{OH}} \times 10^{-4} ) (m³/s)</th>
<th>( R_{\text{BzCl}} \times 10^{-6} ) (kmol/m³ s)</th>
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<td>75.0</td>
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<td>52.628</td>
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**Fig. 2.** Typical consumption of hydroxide solution during an hydrolysis experiment versus time.

**Fig. 3.** Reaction rate versus the sodium hydroxide concentration, for the hydrolysis experiments.
centigrade, respectively. So, for the higher temperatures applied in our study $k_5$ is equal to $k_{3C^2H_5O}$ as defined in Eq. (4). Using these two rate constants ($k_5$ and $k_4$) and the equation for the neutral hydrolysis at saturation point (Eq. (9)) Ohnishi and Tanabe calculated the solubility of benzyl chloride at 4.5, 20 and 30 °C: $V_i = k_{3C^2H_5Cl} + k_{2C^2H_5}$.

So, in order to use this method to calculate the solubility of benzyl chloride at our reaction temperatures, we need two sets of data: firstly, data for the neutral hydrolysis of benzyl chloride at its saturation concentration and, secondly, data for this reaction at a benzyl chloride concentration below the saturation concentration.

In the present work, the solubility of benzyl chloride at 50.0, 64.7 and 75.0 °C was calculated, utilizing the intercept data from Table 2, which represent the value of $k_{3C^2H_5O}$ (the rate of neutral hydrolysis of benzyl chloride at its saturation concentration), and the very precise kinetic data obtained by Robertson and Scott (1961) for the reaction at concentrations below the benzyl chloride saturation concentration. Robertson and Scott (1961) expressed the temperature dependency of the term $k_{3C^2H_5O}$ by the equation:

$$\log(k_{3C^2H_5O}) = -7306.022/T - 19.30921\log(T) + 67.40443$$

(10)

The solubility was calculated by dividing the values of $k_{3C^2H_5O}$ found in the present work by the value of $k_{3C^2H_5O}$ calculated from Eq. (10). The calculated solubilities are given in Table 2 whereas in Fig. 4 the solubility is plotted against the temperature, along with data from Ohnishi and Tanabe (1971) and Olivier (1934). With the solubility the rate constant $k_4$ is calculated from the values of $k_4$ (Table 2).

3.2. Benzylation of starch

The methods and procedures used in studying the benzylation of starch were the same as those applied for the hydrolysis kinetics. Again, the initial slope of the hydroxide consumption graph was used to determine the kinetic parameters and the reaction rate was calculated using Eq. (8). The results of these experiments are given in Table 3 whereas in Fig. 5 the reaction rate is plotted against the hydroxide concentration. The hydroxide concentration was calculated from the measured pH-value and the value of the water dissociation constant at the applied temperature:

$$c_{OH^-} = 10^{-pH - K_w}$$

(11)

The concentration of the RO⁻ species was calculated from: $c_{RO} = c_{OH^-} - c_{OH^{-},e}$ where $c_{OH^{-},e}$ is the hydroxide concentration calculated from the amount of hydroxide put into the system, $c_{OH^{-}{e}}$ the hydroxide concentration present after establishment of the equilibrium given by Eq. (2), $K_w$ the dissociation constant of water. The equilibrium constant $K'$ defined as: $K' = K_{CRHO}/c_{H_2O}$ was calculated utilizing the values of $c_{OH^{-}{e}}$ and $c_{OH^{-},e}$. The intercepts and the slopes of the lines in Fig. 5 give the value for the terms ($k_0 + k_3$) and ($k_4 + k_4'$), respectively (Eq. (4)). The constants $k_4$ and $k_4'$ were determined in the hydrolysis experiments. The constants $k_3$ and $k_4'$ can therefore be calculated utilizing the values from Table 2. Finally, the real rate constants were calculated using the value of the solubility of benzyl chloride and the calculated value $K'$. The results are summarized in Table 3.
Tables 4 and 5. As can be concluded from Table 4, \( k_1 \) is always zero indicating that the direct reaction between starch and benzyl chloride (Eq. (a)) could not be detected under the experimental conditions applied. The experimentally obtained value for the starch dissociation equilibrium constant appears to be independent of temperature, within experimental accuracy. The temperature dependency of the equilibrium constant is given by:

\[
\frac{d \ln K}{dT} = -\frac{\Delta H}{T^2}
\]

So we have indications that \( \Delta H \) is very low for the starch dissociation. The value of \( \Delta H \) for the reaction follows from the difference between the bond enthalpy of the oxygen–hydrogen bond in the starch molecule and water. It is known that the value of the bond enthalpy is approximately the same for any \( \text{OH}^- \) bond, so the more in similar compounds (\( \approx 463 \text{ kJ/mol} \)) (Moore, 1972; Shiver et al., 1990; Weast & Astle, 1981). Therefore, it is not unlikely that \( \Delta H \) is indeed very low, which explains the observed independency of the equilibrium constant with temperature.

Fig. 6 shows the measured reaction rate constants in an Arrhenius graph. From this, the activation energy and the frequency factor of these rate constants were calculated as:

\[
k_2 = 4.21 \times 10^{11} e^{-86.2x10^3/RT}
\]

\[
k_3 = 2.62 \times 10^6 e^{-85.5x10^3/RT}
\]

\[
k_4 = 9.72 \times 10^9 e^{-76.9x10^3/RT}
\]

with \( R = 8.31441 \text{ J/(mol K)} \).

The proposed \( \text{SN}_2 \) reaction mechanism is confirmed by the observed proportionality of the reaction rates to the alkali concentration (Figs. 3 and 5). The values for \( k_2 \) and \( k_4 \) are roughly a thousand times larger than those for \( k_3 \). Both \( k_2/k_4 \) and, to a minor extent, \( k_2/k_3 \) increase with temperature, indicating a positive influence of higher reaction temperatures on the selectivity. The selectivity can also be improved by reducing the amount of water in the reaction mixture. Decrease of the water concentration on one hand reduces the role of reaction (c) in the total reaction, and on the other hand causes an increase in the concentration of the RO\(^-\) species through the equilibrium reaction (f), resulting in an increase in the overall conversion rate of reaction (b). Therefore, it can be concluded that the use of an extruder, in which higher temperatures and lower moisture contents are realizable, indeed offers interesting opportunities for starch benzylation.

### 4. Conclusions

The reactions involved in the homogeneous benzylation of starch in aqueous solutions by benzyl chloride and starch all occur through an \( \text{SN}_2 \) mechanism. The activation energy for reaction between RO\(^-\) and benzyl chloride (reaction (b)) is larger than for the other reactions. The activation energy \( E_a \) is 86.2, 85.5 and 76.9 kJ/mol for reactions (b)–(d), respectively, with reaction (c) the neutral hydrolysis of benzyl chloride and reaction (d) the hydroxide hydrolysis of benzyl chloride. The benzylation of neutral starch (reaction (a)) could not be
detected. Therefore, the selectivity of starch modification relative to benzyl chloride hydrolysis increases with increasing temperature. Selectivity can also be increased through reduction of the water concentration in the reacting system.

The solubility of benzyl chloride in water increased with temperature from $5.14 \times 10^{-3} \text{kmol/m}^3$ at 50°C to $8.21 \times 10^{-3} \text{kmol/m}^3$ at 75°C.

References


