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

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Abstract

The reaction rates in the base-catalysed benzylation of gelatinized aqueous starch (4 wt%), by benzylchloride (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 benzylchloride. The rate equations are:

Starch benzylation : $-R_{\mathrm{BzCl}} = k_2 c_{\mathrm{RO}}^{-} c_{\mathrm{BzCl}}$

Benzylchloride hydrolysis : $-R_{\mathrm{BzCl}} = k_3 c_{\mathrm{OH}}^{-} c_{\mathrm{BzCl}}$

Neutral benzylcholoride hydrolysis : $-R_{\mathrm{BzCl}} = k_4 c_{\mathrm{H_2O}} c_{\mathrm{BzCl}}$

where c_{BzCl} is the benzylchloride concentration, c_{RO}^{-} is the concentration of the dissociated starch hydroxyl group and c_{OH}^{-} is the sodium hydroxide concentration; k is the reaction rate constant. The temperature dependency of the rate constants was measured as:

$$k_2 = 4.21 \times 10^{11}\ \mathrm{e}^{(-86.2\times10^3/RT)}$$

$$k_3 = 2.62 \times 10^{8}\ \mathrm{e}^{(-85.5\times10^3/RT)}$$

$$k_4 = 9.72 \times 10^{9}\ \mathrm{e}^{(-76.9\times10^3/RT)}$$

where $R = 8.31441$ J/(mol K).

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 handeling 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; Maksorov & 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 α-D-glucose, with minor lipid and protein components. The polymers consist

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Nomenclature

BzCl	benzyl chloride ($C_6H_5CH_2Cl$)
BzOH	benzyl alcohol ($C_6H_5CH_2OH$)
c	concentration ($kmol/m^3$)
K	equilibrium constant of starch dissociation
K_w	dissociation constant of water
K'	K [ROH]/[H_2O]
k	reaction rate constant ($m^3/(kmol\ s)$)
k_1''	$k_1[ROH][BzCl]_s$ ($kmol/(m^3\ s)$)
k_2'	$k_2[BzCl]_s$ (1/s)
k_3''	$k_3[H_2O][BzCl]_s$ ($kmol/(m^3\ s)$)
k_4'	$k_4[BzCl]_s$ (1/s)
N	hydroxide solution concentration fed to the system ($kmol/m^3$)
OH^-	hydroxide ions
R_{BzCl}	rate of benzyl chloride production ($kmol/(m^3\ s)$)
RO^-	nucleophilic groups of starch
ROBz	starch benzyl ether
ROH	hydroxyl groups of starch
V_r	the volume of the reaction phase (m^3)
Φ_{OH}	feeding rate of hydroxide solution (m^3/s)
V	rate of neutral hydrolysis (Onishi et al) ($kmol/(m^3\ s)$)

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:

$$\mathrm{ROH} + \mathrm{BzCl} \xrightarrow{k_1} \mathrm{ROBz} + \mathrm{HCl} \tag{a}$$

$$\mathrm{RO}^- + \mathrm{BzCl} \xrightarrow{k_2} \mathrm{ROBz} + \mathrm{Cl}^- \tag{b}$$

$$\mathrm{H_2O} + \mathrm{BzCl} \xrightarrow{k_3} \mathrm{BzOH} + \mathrm{HCl} \tag{c}$$

$$\mathrm{OH}^- + \mathrm{BzCl} \xrightarrow{k_4} \mathrm{BzOH} + \mathrm{Cl}^- \tag{d}$$

$$\mathrm{OH}^- + \mathrm{HCl} \xrightarrow{k_5} \mathrm{H_2O} + \mathrm{Cl}^- \tag{e}$$

Here, ROH represents the hydroxyl groups of the starch molecule, RO^-, the nucleophilic strach groups, OH^-, the hydroxide ions, BzCl, benzyl chloride ($C_6H_5CH_2Cl$), BzOH, benzyl alcohol ($C_6H_5CH_2OH$) 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:

$$\mathrm{OH}^- + \mathrm{ROH} \overset{K}{\leftrightarrow} \mathrm{RO}^- + \mathrm{H_2O} \tag{f}$$

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 then water. In general, acid–base neutralization reactions are instanteneous, (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 (S_N1) and the bimolecular (S_N2) reaction mechanism (Solomons, 1976). In the S_N1 mechanism, the substrate solvolysis is the rate determining step and the reaction rate is dependant on the substrate concentration only. In the S_N2 mechanism, the substrate and the nucleophile react directly via a transition state to form the product. In this case, the rate is dependant on the concentration of both the substrate and the nucleophile.

In general, benzyl chloride reacts with a hydroxyl group either by a S_N1 or a S_N2 mechanism. As shown below, both the benzylation of starch and the competitive reactions of benzyl chloride with water and hydroxide follow the S_N2 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:

$$-R_{BzCl} = c_{BzCl}[k_1c_{ROH} + k_2c_{RO^-} + k_3c_{H_2O} + k_4c_{OH^-}] \tag{1}$$

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 $c_{BzCl,s}$ in water.

Our conclusion is that the neutral hydrolysis of benzyl chloride (reaction (c)) is an S_N2 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 S_N2 mechanism for reaction (d). The dissociation of starch is controlled by the equilibrium constant:

$$K = \frac{c_{RO^-}c_{H_2O}}{c_{ROH}c_{OH^-}} \tag{2}$$

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

$$c_{RO^-} = \frac{c_{ROH}c_{OH^-}}{c_{H_2O}}K \tag{3}$$

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

$$-R_{BzCl}=\left[k_1c_{ROH}+k_3c_{H_2O}+\left(\frac{c_{ROH}}{c_{H_2O}}k_2K+k_4\right)c_{OH^-}\right]c_{BzCl} \tag{4}$$

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:

$$-R_{BzCl}=k_1''+k_3''+(k_2'K'+k_4')c_{OH^-} \tag{5}$$

with:

$$k_1''=k_1c_{ROH}c_{BzCl};\quad k_2'=k_2c_{BzCl};\quad k_3''=k_3c_{H_2O}c_{BzCl};$$
$$k_4'=k_4c_{BzCl};\quad K'=K\frac{c_{ROH}}{c_{H_2O}} \tag{6}$$

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 $(k_2'K'+k_4')$ 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:

$$-R_{BzCl}=k_3''+k_4'c_{OH^-} \tag{7}$$

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_4' 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_{H_2O} 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

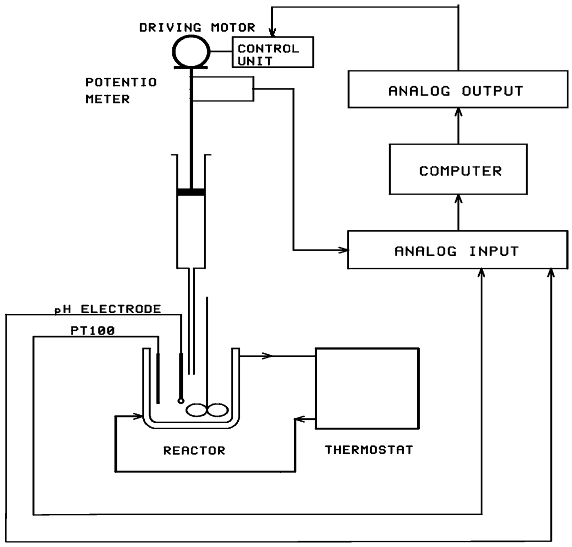

Fig. 1. Experimental setup used for the kinetic measurements.

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:

$$-R_{\mathrm{BzCl}} = \frac{\Phi_{\mathrm{OH^-}} N}{V_{\mathrm{r}}} \tag{8}$$

here Φ_{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 (m^3/s), N, the concentration of the hydroxide solution fed to the system (kmol/m^3) and V_{r}, the volume of the reaction phase (m^3).

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).

$$-R_{\mathrm{BzCl}} = k_3'' + k_4' c_{\mathrm{OH^-}} \tag{9}$$

From Fig. 3, the constants k_4' and k_3'' 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 ($c_{\mathrm{BzCl,s}}$) The neutral hydrolysis rate (V_{s} according to their notation) was measured under these conditions. Secondly, the hydrolysis rate, V is measured at various benzylchloride 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: $V = k_5 c_{\mathrm{BzCl}} + k_6 c_{\mathrm{BzCl}}^2$

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

Experimental conditions and results of the rate determination of the hydrolysis of BzCl

T (°C)	$c_{\mathrm{OH^-}} \times 10^{-3}$ (kmol/m^3)	$\phi_{\mathrm{OH}} \times 10^{-9}$ (m^3/s)	$R_{\mathrm{BzCl}} \times 10^{-6}$ (kmol/m^3 s)
50.0	0.84	1.778	1.149
50.0	3.358	1.871	1.186
50.0	16.777	2.258	1.457
50.0	47.104	3.138	1.971
50.0	62.575	3.748	2.306
64.7	0.000	9.089	5.923
64.7	3.236	9.169	5.934
64.7	6.498	9.260	6.017
64.7	16.461	10.928	7.195
64.7	22.094	12.462	7.564
64.7	32.279	13.361	8.626
64.7	49.990	17.985	11.113
64.7	61.014	18.611	11.355
64.7	63.893	19.586	11.544
75.0	0.000	27.083	17.563
75.0	6.869	29.775	19.185
75.0	16.365	34.192	21.815
75.0	31.422	40.776	25.625
75.0	46.446	44.052	27.280
75.0	60.772	52.628	31.983

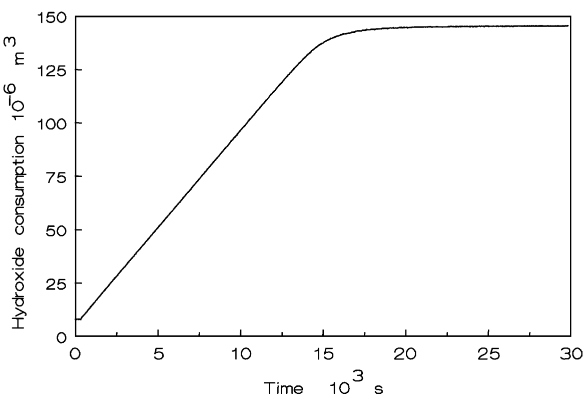

Fig. 2. Typical consumption of hydroxide solution during an hydrolysis experiment versus time.

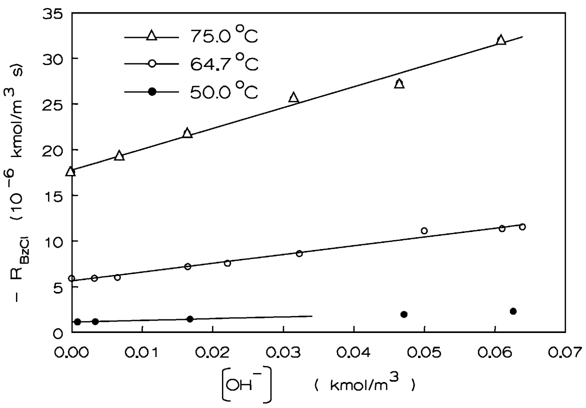

Fig. 3. Reaction rate versus the sodium hydroxide concentration, for the hydrolysis experiments.

Table 2
Results of the hydrolysis experiments

T (°C)	$k_3'' \times 10^{-6}$ (kmol/m^3 s)	$k_4' \times 10^{-5}$ (1/s)	$k_3 \times 10^{-6}$ (m^3/kmol s)	$k_4 \times 10^{-3}$ (m^3/kmol s)	$c_{BzCls} \times 10^3$ (kmol/m^3)
50.0	1.13	1.85	4.04	3.63	5.14
64.7	5.63	9.61	15.4	14.3	6.74
75.0	17.8	22.8	40.0	27.7	8.21

centigrade, respectively. So, for the higher temperatures applied in our study k_5 is equal to $k_3 c_{H_2O}$ as defined in Eq. (4). Using these two rate constants (k_5 and k_6) 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: $V_s = k_5 c_{BzCl,s} + k_6 c_{BzCl,s}^2$

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 $k_3 c_{H_2} c_{BzCls}$ (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 $k_3 c_{H_2O}$ by the equation:

$$\log(k_3 c_{H_2O}) = -7306.022/T - 19.3092 \log(T) + 67.40443 \tag{10}$$

The solubility was calculated by dividing the values of $k_3 c_{H_2O} c_{BzCls}$ found in the present work by the value of $k_3 c_{H_2O}$ 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).

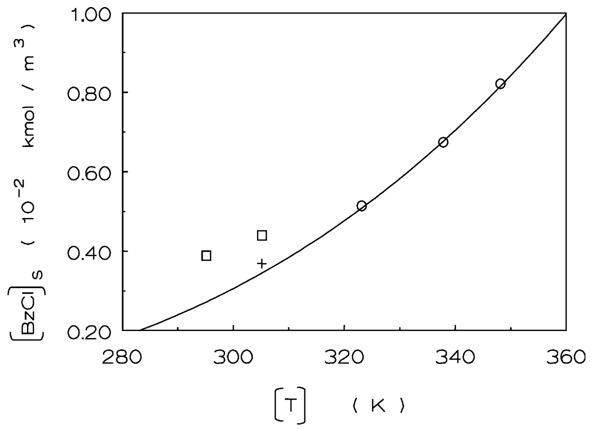

Fig. 4. The solubility of benzyl chloride in water plotted against the temperature. Data: ○ this work; + Olivier (1934); ☐ Ohnishi and Tanabe (1971).

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:

$$c_{OH^-} = 10^{-(K_w + pH)} \tag{11}$$

The concentration of the RO$^-$ species was calculated from: $c_{RO^-} = c_{OH^-,o} - c_{OH^-,e}$ inhere $c_{OH^-,o}$ 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: $K' = K c_{ROH}/c_{H_2O}$ was calculated utilizing the values of $c_{OH^-,e}$ and $c_{OH^-,o}$. The intercepts and the slopes of the lines in Fig. 5 give the value for the terms ($k_1'' + k_3''$) and ($k_2' K' + k_4'$), respectively (Eq. (4)). The constants k_3'' and k_4' were determined in the hydrolysis experiments. The constants k_1'' and $k_2' K'$ 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
Experimental conditions and results of the rate determination of starch benzylation

T (°C)	$c_{OH} - ,e \times 10^{-3}$ (kmol/m^3)	$\phi_{OH} \times 10^{-9}$ (m^3/s)	$R_{BzCl} \times 10^{-6}$ (kmol/(m^3 s))	K
50.0	0.01	1.502	1.07	
50.0	5.888	2.179	1.455	82.6
50.0	9.12	2.567	1.688	120.7
50.0	16.596	3.463	2.356	110.4
50.0	17.783	3.468	2.299	150
64.7	1.035	8.641	5.845	98.3
64.7	2.541	9.092	6.111	83.5
64.7	10.116	14.75	9.63	101.4
64.7	15.668	17.743	11.363	95
75.0	0.093	24.324	17.099	
75.0	2.512	28.021	19.439	98.1
75.0	5.623	36.416	24.935	104.1
75.0	10.471	39.323	26.886	109.5
75.0	14.454	48.091	32.561	88.7

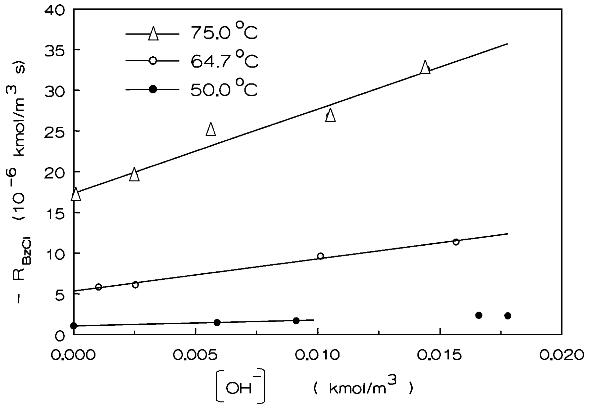

Fig. 5. The reaction rate versus the sodium hydroxide concentration, for the benzylation experiments.

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:

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{-\Delta H}{T^2} \tag{12}$$

So we have indications that ΔH is very low for the starch dissociation. The value of ΔH 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 OH$^-$ bond, so the more in similar compounds (≈463 kJ/mol) (Moore, 1972; Shiver et al., 1990; Weast & Astle, 1981). Therefore, it is not unlikely that ΔH is indeed very low, which explains the observed independency of the equilibrium constant with temperature.

Table 4
Intermediate results of the benzylation and hydrolysis experiments

T (°C)	Hydrolysis		Benzylation	
	$k''_3 \times 10^{-6}$ (kmol/m^3 s)	$k'_4 \times 10^{-3}$ (1/s)	$k''_1 + k''_3 \times 10^{-6}$ (kmol/(m^3 s)	$k'_2 + k'_4K' \times 10^{-5}$ (1/s)
50.0	1.13	1.85	1.04	7.37
64.7	5.63	9.61	5.34	39.5
75.0	17.8	22.8	17.5	103

Table 5
Reaction rate constants and equilibrium constant determined from the results of the benzylation and hydrolysis experiments

T (°C)	$k_2 \times 10^{-3}$ (m^3/kmol s)	$k_3 \times 10^{-6}$ (m^3/kmol s)	$k_4 \times 10^{-3}$ (m^3/kmol s)	K
50.0	4.71	4.04	3.64	116
64.7	21.1	15.4	14.3	95
75.0	46.4	40.0	27.7	100

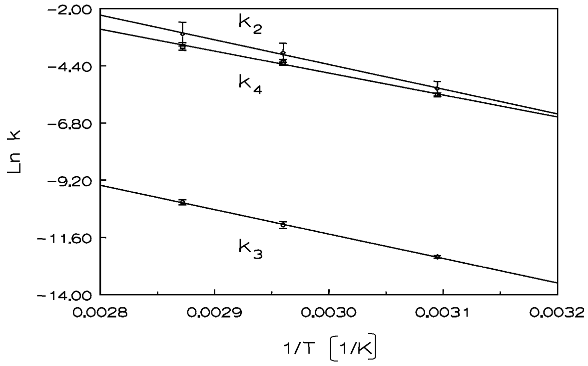

Fig. 6. Arrhenius graph for the measured rate constants.

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:

$$k_2 = 4.21 \times 10^{11}\ \mathrm{e}^{(-86.2\times10^3/RT)} \tag{13}$$

$$k_3 = 2.62 \times 10^{8}\ \mathrm{e}^{(-85.5\times10^3/RT)} \tag{14}$$

$$k_4 = 9.72 \times 10^{9}\ \mathrm{e}^{(-76.9\times10^3/RT)} \tag{15}$$

with $R = 8.31441$ J/(mol K)

The proposed S$_N$2 reaction mechanism is confirmed by the observed proportionality of the reaction rates to the alkali concentration (Figs. 3 and 5). The values for k_2 and k_4 are roughly a thousand times larger then those for k_3. Both k_2/k_4 and, to a minor extent, k_2/k_3 increase with temperature, indicating a positive influence of higher reaction temperatures on the selectivity. The selectivity can also be improved by reducing the amount of water in the reaction mixture. Decrease of the water concentration on one hand reduces the role of reaction (c) in the total reaction, and on the other hand causes an increase in the concentration of the RO$^-$ 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 S$_N$2 mechanism. The activation energy for reaction between RO$^-$ 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 5.14×10^{-3} kmol/m^3 at 50 °C to 8.21×10^{-3} kmol/m^3 at 75 °C.

References

Asahina, T., & Nara, G. (1934). Preparation of benzyl esters. *Bulletin of Chemistry Society of Japan*, *9*, 530.

Beste, G. W., & Hammett, L. P. (1940). Rate and mechanistics in the reaction of benzyl chloride with water, hydroxyl ions and acetate ions. *Journal of American Chemistry Society*, *62*, 2481.

Doppert, H. L., & Staverman, A. J. (1966). Polyelectrolytic character of amylose. *Journal of Polymer Science*, *4*, 2367.

Golinkin, H. S., & Hyne, J. B. (1968). Enthalpy and entropy of activation for benzylchloride solvolysis in various alcohols and water solvent mixtures. *Canadian Journal of Chemistry*, *46*, 125.

Gomberg, M., & Buchler, C. C. (1921). Preparation of benzyl esters and of benzyl derivatives from benzylchloride. *Journal of American Chemistry Society*, *43*, 1904.

de Graaf, R. A., & Janssen, L. P. B. M. (2000). The production of a new partially biodegradable starch plastic by Reactive Extrusion. *Polymer Engineering and Science*, *40*(9), 2086–2094.

de Graaf, R. A., Broekroelofs, G. A., Janssen, L. P. B. M., & Beenackers, A. A. C. M. (1995). The kinetics of the acetylation of gelatinised potato starch. *Carbohydrate Polymers*, *28*, 137–144.

de Graaf, R. A., Broekroelofs, G. A., & Janssen, L. P. B. M. (1998). The acetylation of starch by reactive extrusion. *Starch/Stärcke*, *62*, 10–120.

Homan Free, H. W., Joosten, G. E. H., Roelfsema, W. A., & Stamhuis, E. J. (1985). The heterogeneous kinetics of the benzylation of suspended starch. *Starch*, *37*, 14.

Maksorov, B. V., & Andrianov, K. A. (1933a). Use of benzanyloic resins for the productions of plastics. *Plasticheskir Massy*, *6*(1).

Maksorov, B. V., & Andrianov, K. A. (1933b). *Chimie and Industry*, *32*(404).

Maksorov, B. V., & Andrianov, K. A. (1934). *Chemistry Abstracts*, *28*, 7041.

Maksorov, B. V., & Andrianov, K. A. (1935). Preparation of artificial resins from starch and starchy materials. *Rev.Gen. Mat. Plastiques*, *11*(336), 275.

Maksorov, B. V., & Andrianov, K. A. (1936). Preparation of artificial resins from starch and starchy materials. *Chemistry Abstracts*, *30*, 6083.

Moore, W. J. (1972) (4th ed.). *Physical chemistry*, p. 279; Longman, London.

Moser, K. B. (1987). In O. B. Wurzburg (Ed.), *Modified starches: Properties and uses*. Boca Raton, FL: CRC Press.

Ohnishi, R., & Tanabe, K. (1971). Mechanistics in the reaction of benzyl chloride with water. *Bulletin of Chemistry Society of Japan*, *41*, 2647.

Olivier, S. C. J. (1934). Influence of the nature of the solvent on the catalytic power of hydroxide ions in hydrolysis. *Rec. Trav. Chim*, *53*, 891.

Olivier, S. C. J., & Weber, A. P. H. (1934). The constitution of the substrate and its sensitivitiness to the hydroxide ion in hydrolysis. *Rec. Trav. Chim*, *53*, 869.

Robertson, R. E., & Scott, J. M. W. (1961). Neutral hydrolysis of some allyl and benzyl halides. *Journal of Chemistry Society*, 1596.

Shiver, D.F., Atkins, P.W., Langford, C.H (1990). Inorganic chemistry, Whiley, Oxford.

Solomons, T. W. (1976). *Organic chemistry*. New York: Wiley, p. 630.

Swain, C. G., & Scott, C. B. (1953). *Journal of American Chemistry Society*, *75*, 141.

Tanabe, K., & Sano, T. (1962). *Journal of Research Institute of Catalysis, Haikkado University*, *10*(2), 173–182.

Weast, R. C., & Astle, M. J. (Eds.), (1981). *Handbook of chemistry and physics* (62nd ed). Boca Raton, FL: CRC Press.

Wurtzburg, O. B. (1986). *Modified starcher: Properties and uses*. Boca Raton, FL: CRC Press, pp. 1–300.