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On the Reaction of Potato Starch with Isocyanates

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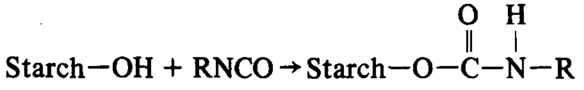
SUMMARY

The reactions of potato starch in aqueous suspension with some isocyanates were investigated. In contrast to previously reported results we found that no starch carbamates were formed but only the corresponding urea compounds. These urea compounds were physically bound to the potato starch and could be washed from the starch by several organic solvents.

INTRODUCTION

As part of our research on potato starch derivatives the reaction of potato starch with phenyl, n-butyl and cyclohexyl isocyanate was studied. It is well known that isocyanates react with alcohol (Satchell & Satchell, 1975) and their reaction with starch is also described in the literature (Wolff, 1951, 1964; Wolff *et al.* 1954; Roberts, 1965), i.e.



$$\mathrm{Starch{-}OH + RNCO \rightarrow Starch{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}R} \qquad (1)$$

These literature references refer to the original work of Wolff, Watson and Rist, who describe the reaction of starch granules with several isocyanates in aqueous medium (Wolff *et al.*, 1954) and in pyridine

(Wolff & Rist, 1948; Wolff *et al.*, 1952, 1954). To avoid the obvious disadvantages of the pyridine medium in commercial practice, we carried out the reaction in aqueous suspension as described by Wolff *et al.* (1954).

Potato starch was reacted with varying levels of phenyl isocyanate (0·11–0·44 mole per anhydroglucose unit) at room temperature for about 3½ h. The Degree of Substitution (DS), defined as the number of carbamate groups in the starch per anhydroglucose unit, was calculated from the carbon to nitrogen ratio obtained from elemental analysis of the products. This method of determination does not require a completely dry sample because water does not affect the C/N ratio. Therefore the analytical data reported was not obtained from the anhydrous p.a. products.

The determination of the DS has to be corrected for any nitrogen present in the native starch; however, analysis of the potato starch used by us showed that it contained no detectable amounts of nitrogen. Table 1 shows the analytical data obtained for the products and the DS values calculated from this data. The DS values reported in the tables are calculated on the assumption that the nitrogen in the product originates from a carbamate substituent.

From the data in Table 1 it seems at first sight that all the added isocyanate reacts with the starch. The products formed in the reaction had an increasing amorphous appearance with increasing nitrogen content, which is in agreement with the results reported by Wolff *et al.* (1954).

TABLE 1

Analytical Data and Calculated DS of the Products Obtained from Potato Starch with Phenyl Isocyanate

Moles phenyl isocyanate added per mole anhydroglucose unit	*Analysis of the product*		*Calculated DS*
	%C	*%N*	
0·11	44·69	0·88	0·11
0·22	46·91	1·62	0·22
0·33	47·48	2·08	0·31
0·44	49·03	2·81	0·45

The reaction of potato starch with n-butyl isocyanate required 6 h at 55°C to go to completion and the reaction with cyclohexyl isocyanate needed 24 h at 55°C. These figures are consistent with the reported reactivities of isocyanates with hydroxyl groups (Arnold *et al.*, 1957). We subjected the products to a closer examination, starting with the ones formed by the reaction of potato starch with phenyl isocyanate. They were washed with organic solvents. When methanol, acetone or ether was used, material was found to dissolve and to pass through the filter. After evaporation of the solvent from the filtrate, the residue showed an IR spectrum which closely resembled that of the starting product. From elemental analysis it appeared that the percentage of nitrogen in the starch product on the filter after washing with methanol, acetone or ether had fallen considerably which would indicate a decrease in DS (Table 2). Washing with benzene had a smaller effect.

The residue in the filtrate was subjected to elemental analysis. The percentage of carbon and nitrogen was considerably higher than found in the starch product before washing. To elucidate the structure of the compound in the residue of the filtrate a mass spectrum was taken. This showed a M^+ peak at *m/e* 212 and two strong peaks at *m/e* 119 and 93. These data are in agreement with those of diphenylurea, which has a molecular weight of 212.

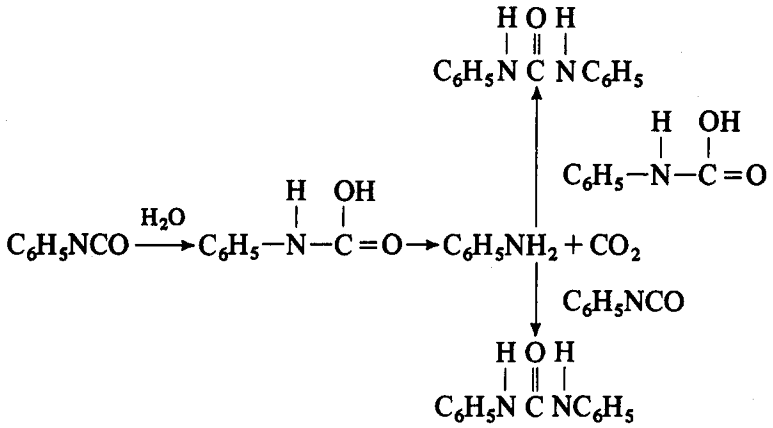
TABLE 2

Analytical Data and Calculated DS of the Products after Washing with Organic Solvents

Washing solvent	*Entry**	*Moles phenyl isocyanate per mole anhydroglucose unit*	*Analysis of the washed product*		*Calculated DS after washing*
			%C	*%N*	
Methanol	(a)	0·22	43·75	0·92	0·12
Acetone	(b)	0·22	43·65	0·31	0·04
Ether	(c)	0·22	44·95	1·34	0·19
Ether	(d)	0·30	42·65	0·64	0·08
Benzene	(e)	0·30	45·87	1·82	0·27

* For the explanation of the entry numbers see the experimental section.

Diphenylurea can be formed by the reaction of phenyl isocyanate with water. First the isocyanate reacts with water to form a carbamic acid which decomposes to aniline and CO_2 (Satchell & Satchell, 1975).



$$C_6H_5NCO \xrightarrow{H_2O} C_6H_5{-}N(H){-}C(OH){=}O \rightarrow C_6H_5NH_2 + CO_2$$

$$C_6H_5NH_2 \xrightarrow{C_6H_5{-}N(H){-}C(OH){=}O} C_6H_5NH{-}C(=O){-}NHC_6H_5$$

$$C_6H_5NH_2 \xrightarrow{C_6H_5NCO} C_6H_5NH{-}C(=O){-}NHC_6H_5$$

Aniline can react either with another molecule of the carbamic acid or with phenyl isocyanate (Arnold *et al.*, 1957) to form the diphenylurea.

We suggest that the diphenylurea is physically bound to the starch. It is removed from the starch by washing with an organic solvent. To test this hypothesis, potato starch was stirred in water with diphenylurea. In this experiment a homogeneous product was obtained having identical properties (IR, elemental analysis, appearance) to the material obtained in the reaction of potato starch with phenyl isocyanate. The fact that washing the starch with benzene has a smaller effect than with the other solvents (Table 2) can be explained by the higher solubility of diphenylurea in ether compared with benzene (Weast, 1977). The extraction with methanol and acetone proceeds more rapidly than with ether, although the solubility of the urea compound is higher in the latter solvent. This probably is due to the fact that acetone and methanol penetrate into the water-wet starch much more easily.

To investigate whether only diphenylurea is produced or whether a substantial amount of the desired starch carbamate was formed, the reacted potato starch was subjected to continuous extraction in a Soxhlet apparatus using ether as extracting liquid. The results of this experiment are shown in Table 3.

It is clear that nearly all the phenyl isocyanate is converted into diphenylurea. The starch obtained after extraction showed an IR

TABLE 3
Analytical Data and Calculated DS of the Product after Extraction with Ether

Extraction time in hours	*Analysis of the product* after extraction*		*Calculated DS*
	%C	*%N*	
0	46·61	1·99	0·30
24	42·38	0·21	0·03
168	42·22	0·10	0·01

* The experiment was carried out using 0·3 mole phenylisocyanate per mole anhydroglucose unit.

spectrum which was identical to the spectrum of the native starch. This shows that the properties of the starch have not been altered by the apparent reversible physical absorption of the uream compound.

In the reactions of potato starch with n-butyl isocyanate and cyclohexyl isocyanate in aqueous medium, the corresponding urea compounds were formed in an analogous way to the reaction with phenyl isocyanate. These urea compounds were again found to be physically bound to the potato starch and could be washed out by the organic solvent.

Our conclusion is that no starch carbamates are formed in the reactions of potato starch with phenyl, n-butyl and cyclohexyl isocyanate in aqueous suspension. Only the corresponding urea compounds are formed which are physically bound to the potato starch and which can be washed from the starch by organic solvents.

EXPERIMENTAL

General

Phenyl isocyanate, n-butyl isocyanate and cyclohexyl isocyanate were purchased from Aldrich. The potato starch was obtained from AVeBe, Veendam, The Netherlands. The IR spectra were determined on a Perkin Elmer 177 infrared spectrophotometer. The IR spectra of the solid materials were taken as an emulsion in nujol. The elemental analyses were performed in the Micro-analytical Department of this Laboratory. Mass spectra were recorded on an AEI MS9 mass spectrometer in the Department of Organic Chemistry.

Reaction of potato starch with phenyl isocyanate in water

A suspension of 10 g potato starch (containing 12% water) in 40 ml water was brought to pH 11 with 0·25 N NaOH. Phenyl isocyanate was added and the solution was stirred at room temperature for 3½ h. The solid material was collected by filtration, washed several times with water and dried.

IR: 3680–2380, 3330, 3280, 1645, 1595, 1555, 1315 and peaks between 1295 and 700 cm^{-1}.
Elemental analysis: see Table 1.

The reaction product was washed with either methanol (175 ml, entry (a)) or acetone (100 ml, entry (b)) or ether (100 ml, entry (c)). In other experiments the product was first stirred for about 2 h in either 50 ml ether (entry (d)) or 50 ml benzene (entry (e)) and thereafter washed with 700 ml of the solvent. The analytical data are summarized in Table 2. In other experiments the starch products obtained in the reaction of potato starch and 0·3 equivalent phenyl isocyanate were subjected to continuous extraction with ether in a Soxhlet apparatus for 24 h and 168 h respectively. The analytical data are summarized in Table 3.

IR: 3720–2360, 1745–1590, 1160, 980, 860, 725 cm^{-1}.

The solvent was removed from ether solution on a rotary evaporator leaving the residue.

IR: 3330, 3280, 1645, 1595, 1550, 1315 and peaks between 1295 and 700 cm^{-1}.
Analysis: C 73·20%, N 13·01%.
Exact mass for $C_{13}H_{12}N_2O$: theoretical 212·095, experimental 212·096.

From the original potato starch an IR spectrum was taken:

IR: 3680–2320, 1740–1580, 1155, 975, 855, 725 cm^{-1}.

Reaction of potato starch with diphenylurea

To a suspension of 10 g potato starch (containing 13% water) in 40 ml water 1 g diphenylurea was added. The solution was stirred at room temperature for 3 h. Thereafter the solid material was collected by filtration, washed with water and dried.

IR: 3680–2360, 3320, 3270, 1645, 1595, 1555, 1315 and peaks between 1235 and 700 cm^{-1}.
Analysis: C 43·03%, N 1·44%.

Reaction of potato starch with n-butyl isocyanate

10 g potato starch (containing 13% water) was suspended in a solution of 16 g sodium sulphate in 40 ml water. The suspension was brought to pH 11 with 0·25 N NaOH. n-Butyl isocyanate was added, the suspension was brought to 55°C and stirred at this temperature for 6 h. After cooling to room temperature the solid material was collected by filtration, washed thoroughly with water and dried.

IR: 3660–2360, 3320, 1615, 1575 and peaks between 1270 and 720 cm^{-1}.
Analysis: C 43·86%, N 1·66%.

The product obtained was stirred at room temperature for 1 h in 100 ml ether and thereafter washed with 750 ml ether.

IR: 3720–2350, 1740–1590, 1155, 975, 860, 725 cm^{-1}.

From the combined ether layers the ether was removed on the rotary evaporator to leave the residue.

IR: 3320, 1615, 1575, 1275, 1230, 1075, 1030, 720 cm^{-1}.
Analysis: C 62·68%, N 16·42%.
Exact mass for $C_9H_{20}N_2O$: theoretical 172·158, experimental 172·160.

Reaction of potato starch with cyclohexyl isocyanate

10 g potato starch (containing 13% water) was suspended in a solution of 16 g sodium sulphate in 40 ml water. The suspension was brought to pH 11 with 0·25 N NaOH, heated to 55°C and cyclohexyl isocyanate

(0·3 eq) was added. The suspension was stirred at 55°C for 24 h. After cooling to room temperature the solid material was collected by filtration, washed thoroughly with water and dried.

IR: 3660–2340, 3320, 1625, 1575, 1310 and peaks between 1245 and 725 cm^{-1}.
Analysis: C 45·62%, N 1·49%.

The compound obtained was subjected to continuous extraction with ether in a Soxhlet apparatus for 24 h. Starch residue:

IR: 3740–2360, 1740–1590, 1160, 980, 855, 725 cm^{-1}.
Analysis: C 42·75%, N 0·57%.

From the ether solution the ether was removed on a rotary evaporator to leave the residue.

IR: 3320, 1625, 1575, 1310, 1245, 1090, 895 cm^{-1}.
Analysis: C 69·48%, N 11·73%.
Exact mass for $C_{13}H_{24}N_2O$: theoretical 224·189, experimental 224·189.

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