Application of the Maillard, Strecker and modified Strecker (P-Mannich) reactions for the chemical modifications of wool

Lajos Trézl*, Csaba Vida, Imre Petneházy, István Rusznák, Péter Bakó and László Tőke

Dept of Organic Chemical Technology, Technical University of Budapest, PO Box 91, Budapest H-1521, Hungary

The application of the Maillard, Strecker and modified Strecker reactions in the chemical modification of wool are described. A practical method for improving reactive or acid dye pick-up under milder conditions of wool dyeing was the aim of the present work. This can be achieved by means of chemical bonding of selected carbohydrates with wool.

INTRODUCTION

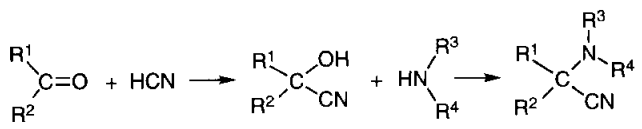
Chemical modification of wool, enabling enhanced dye pick-up under relatively mild process conditions, has been studied for decades; theoretical and practical results have recently been published [1,2]. One practical goal of the work was the modification of the structure of wool, enabling it to be dyed at low temperatures, exploiting its ability to undergo certain chemical reactions [3,4].

The desired improved dyeability of wool has been achieved initially via interaction with a glucose derivative crown ether. Cross-linking in wool caused by the Maillard reaction has been verified as the process responsible for modifying the fibre structure. Optimised conditions have also been established for the Maillard reaction. The incorporation of carbohydrates to loosen the fibre structure and build in special functional groups in order to economise on dye consumption at lower temperature was another goal.

Based upon experiences with the Maillard reaction, further chemical reactions have been sought to enable introduction of carbohydrate molecules into the chemical structure of wool. The reaction of organic oxo compounds with cyanides was chosen as the first such process [5,6].

In 1850 details of the reaction of different cyanohydrins with primary and secondary amines were published by Strecker (Scheme 1) [7]. The exceptional reactivity of cyanohydrins meant that they could react with amino acids and proteins. The formation of a glucose-cyanohydrin species in reaction between glucose and the cyanide ion was disclosed by Fischer [8], and the high reactivity of this compound demonstrated by quantum chemical calculations [6].

It was decided to incorporate glucose into wool keratin in the form of glucose-cyanohydrin at a lower temperature and in shorter time than could be achieved by the Maillard reaction itself. This, it was thought, should



R^1 = alkyl, aryl
R^2, R^3, R^4 = H, alkyl, aryl

Scheme 1

*To whom correspondence should be addressed

be possible if highly reactive cyanohydrins were used (Scheme 2).

The relatively low temperature and short duration of the Strecker reaction allowed a single-bath procedure for successive pretreatment and dyeing to be adopted. It was recognised that the application of cyanides in a dyehouse would face several obstacles, although the huge excess of glucose used in the system would considerably reduce the dangers. Nevertheless, another compound, much less harmful to health than cyanides, had to be found. This led to an examination of modification to the Strecker reaction (the P-Mannich reaction) in which dimethyl phosphite replaces cyanide (Schemes 3 and 4) [9]. This reaction is used for producing α-aminophosphonic acids but it previously had not been extended to interactions with glucose.

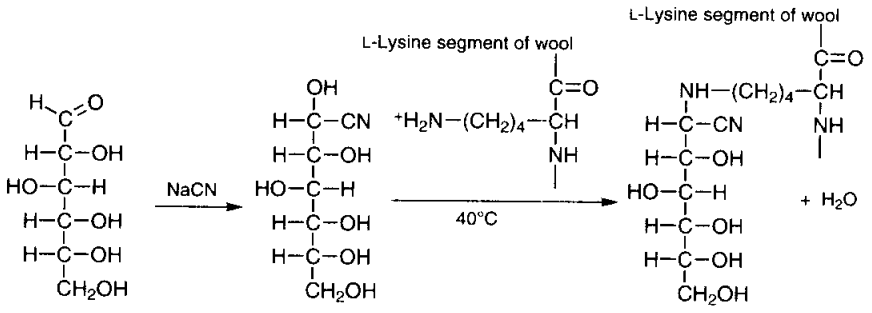
During the reaction mobile hydrogen from the dimethyl phosphite molecule is first removed in a base-catalysed process. The negative ion produced can react in a similar way to the cyanide ion, at the carbon atom of the aldehyde group of glucose. The next step is the formation of *N*-phosphonoglucosyl lysine in a nucleophilic substitution reaction. As in the Strecker and Maillard reactions, the modified Strecker reaction is also able to build reductive carbohydrates into wool keratin by covalent bond formation.

EXPERIMENTAL

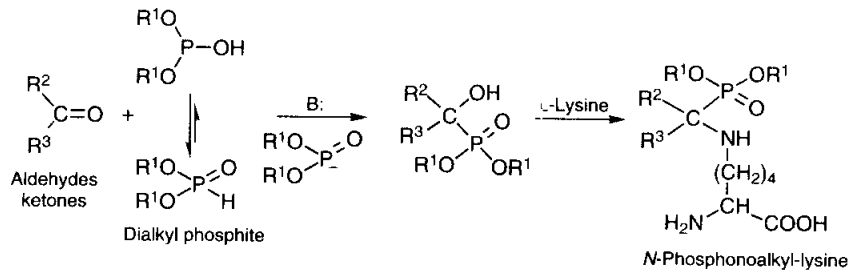
Treatments and the tests of the samples were carried out on Australian combed wool sliver using a concentration of 0.05 mol/l glucose, sodium cyanide and dimethyl phosphite in treatments A–D (Table 1). The times and temperatures of treatment were as shown in Table 1. Dye penetration and colour measurement were tested on woven fabric. Control treatments in distilled water were also carried out. The method of Caldwell *et al.* was used to check performic acid/ammonia solubility [10]. Tensile strength and elongation at break were determined using a Computex FM-27. Scanning electron microscopic pictures were obtained by a Jeol ISM-35 device.

Dyeing procedure

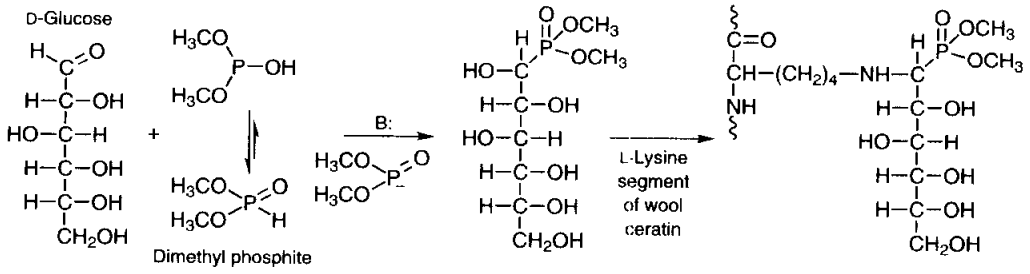
Dyeing was carried out in a Dyeing Tester FE-08/B laboratory machine. The dyebath contained 1% o.w.f. nonionic surfactant, 10% o.w.f. sodium sulphate (for acid dye) or 4% o.w.f. ammonium sulphate (for reactive dye), together with acetic acid to pH 5.0; the liquor ratio was



Scheme 2



Scheme 3



Scheme 4

Table 1 Change in diameter of wool fibres after treatment (Lanameter FM-02; average of 200 determinations)

Treatment[a]	Fibre diameter (μm)
Untreated	17.7
Blank	18.3
A	18.7
B	18.9
C	19.2
D	18.6

a *Treatments*
A Maillard reaction: glucose for 30 min at 90°C
B Strecker reaction: glucose plus sodium cyanide for 20 min at 40°C
C Modified Strecker reaction: glucose plus dimethyl phosphite for 30 min at 80°C
D Dimethyl phosphite for 30 min at 80°C

30:1. Blank and pretreated wool fabric samples were treated in this solution for 10 min at 40°C. Dye (0.2–2.0% o.w.f.) was then added to the dyebath, and the temperature was raised at a rate of 2 degC/min to 80°C, and the dyeing procedure continued for a further 60 min. Dyeing was followed by rinsing in hot water, soaping for 30 min at 60°C, with final washing in water before drying. The colour strength of the dyed samples was determined using a Datacolor ICS-3000 colorimeter in terms of measured reflectance values R and expressed as K/S values by means of the Kubelka–Munk equation [11].

Dyed wool samples were extracted with a 1:1 mixture of dimethyl formamide (DMF) and water for 30 min at boiling point.

Colour and light fastness testing

Fastness testing was carried out according to BS 1006/ISO 105 standard methods. The specific tests used were C04 colour fastness to washing, E04 colour fastness to perspiration, D02 colour fastness to rubbing and B08 colour fastness to light.

Light microscopic investigations

The uniformity of dye penetration uniformity in dyed samples was analysed by light microscopy (Carl Zeiss, Option 10).

Quantum chemical calculations

Some reactions and their effects could not be interpreted by classical chemical concepts, especially in the case of charge distribution in alkylated phosphines and glucose-cyanohydrin. So it was decided to apply quantum chemical calculations. The calculations were conducted using Silicon Graphics Iris Indigo 2 workstation. A Gaussian 92 algorithm was used to determine the 6–31 G* electrostatic potential derived point charges. The semi-empirical electrostatic potential derived point charges were obtained using the MNDO Hamiltonian. The geometries of molecules were fully optimised with the split-valence 3–21G basis set.

Mulliken's complete atom population was calculated using Eqn 1:

$$Q_A = \sum_{\mu \in A} n_\mu = \sum_{\nu \in A} \sum_{\mu=1}^{m} D_{\nu\mu} S_{\nu\mu} = d_A + \sum_B d_{AB} \qquad (1)$$

where Q_A = atomic charge
$d_A = \sum_{\mu,\nu \in A} D_{\nu\mu} S_{\nu\mu}$ = net electron population:
$d_{AB} = \sum_{\mu \in A} \sum_{\nu B} D_{\nu\mu} S_{\mu\nu}$ = Mulliken's overlap population.

The electrostatic potential map was calculated using Eqn 2:

$$V(r) = \sum_A \frac{Z_A}{R_A - \bar{r}} - \int \frac{\rho(\bar{r}')\, d\bar{r}'}{\bar{r}' - \bar{r}} \qquad (2)$$

where Z_A = charge of nucleus
R_A = position of nucleus
$\rho(\bar{r}')$ = electron density function.

RESULTS AND DISCUSSION

Changes in fibre diameter and physico-mechanical properties

Treatments were expected to increase fibre diameter, and indeed tests showed a slight increase in diameter (Table 1). The increase in fibre diameter could raise the rates of dye penetration and diffusion. Consequently the time needed to achieve good quality dyeings could be reduced. Neither physico-mechanical properties nor performic acid/ammonia solubility deteriorated after treatment (Table 2). In agreement with these results, scanning electron microscopic tests did not show any damage in the scale structure.

Amino acid and IR analysis

Amino acid analysis (Beckmann 6300 amino acid analyser) was used to verify covalent bond formation between the applied treatment agents and the amino and guanidine groups in wool. The objective of the test was to define changes in lysine and arginine content of the treated

Table 2 Changes in wool properties after treatment (tensile strength and elongation average of 100 measurements)[a]

Treatment	Performic acid/ammonia solubility (%)	Tensile strength (cN)	Elongation at break (%)
Blank	63.2	7.68	42.4
A	61.2	7.85	41.9
B	62.8	7.73	42.0
C	63.1	7.87	41.8

a For key see Table 1

samples compared with that of untreated wool. The lysine, arginine and hystidine content decreased by 13–26% due to the treatments (Table 3). IR spectroscopic analysis also showed significant differences between the spectra of treated and untreated samples at various vibrational frequencies, further evidence for the reactions between wool and treatment agents.

Table 3 Amino acid analysis of blank and treated wool samples

	Amino acid content (mmol/g wool)		
Treatment	Histidine	Lysine	Arginine
Blank	68	216	597
A	53	189	513
B	50	181	509
C	51	177	495

a For key see Table 1

Effect on acid and reactive dye pick-up

The reaction of glucose molecules with the accessible amino groups of wool should reduce the dye pick-up of the fibre if there were not an opening up of the wool structure occurring simultaneously. This latter process causes the number of accessible sites to increase markedly, bringing about enhanced dye pick-up.

Using the dichlorotriazine reactive dye (CI Reactive Red 2) and the acid dye (CI Acid Red 118) selected for this study, an increase in dye pick-up was noted for all three modifying reactions with wool. The efficiency of the treatments decreased in the following order: modified Strecker > Strecker > Maillard, although differences in the *K/S* values of the three differently modified samples were very slight. In the case of reactive dye fixed to wool by covalent bonding (not released after extraction with DMF/water mixture) differences could be observed between the modified and the blank samples. The improved quality and uniformity of dyeing were indicated by light microscopic studies of the modified wool sample after dyeing.

Changes in colour and light fastness

As Tables 4–6 indicate, the colour and light fastness properties did not decrease with the chemical modifications to wool. It seemed that the glucose pretreatment (Maillard reaction) brought about a slight improvement in dye fastness.

Comparison of the modification reactions

In the Maillard reaction, conducted for 30 min at 90°C, the glucose molecule reacted with accessible amino and guanidine groups at quite high temperatures. Ionic and secondary bonds in wool were broken, and further reaction of glucose molecules with the newly accessible functional groups of the fibre occurred.

In the Strecker reaction, conducted for 20 min at 40°C, the steps were identical to the Maillard reaction, except that glucose-cyanohydrin was the modifying agent. Quantum chemical calculations showed that this reaction is energetically much more favoured than that with glucose, because the C^2 carbon atom in Figure 1 (with an attached nitrile group) has a considerable partial positive

Table 4 Fastness properties after treatment of dyeings with CI Acid Red 118[a,b]

	C04			E04			D02	
Treatment	CS	SC	SW	CS	SC	SW	SC (dry)	SC (wet)
Blank	4	3–4	4	4	2–3	3	3–4	3–4
A	4–5	4	4–5	4	3	4	4	4
B	4–5	3–4	4	4	2–3	3–4	4	3–4
C	4–5	4	4	4	3	4	4	4

a For key see Table 1
b CS – change of shade, SC – staining of cotton, SW – staining of wool

Table 5 Fastness properties after treatment of dyeings with CI Reactive Red 2[a]

	C04			E04			D02	
Treatment	CS	SC	SW	CS	SC	SW	SC (dry)	SC (wet)
Blank	5	4	4	4–5	3–4	3–4	4	4
A	5	4–5	4–5	5	4–5	4	4–5	4
B	5	4	4	4–5	4	3–4	4	4
C	5	4	4	5	4–5	4	4	4

a For key see Tables 1 and 4

Table 6 Light fastness after treatment[a]

	B08	
Treatment	CI Acid Red 118	CI Reactive Red 2
Blank	5	6
A	6	7
B	5–6	6
C	5–6	6–7

a For key see Table 1

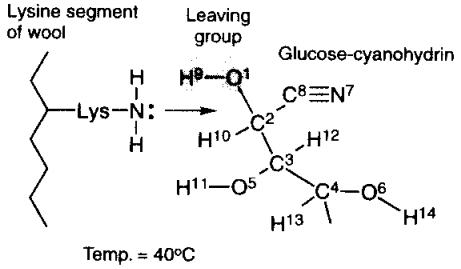


Figure 1 Net atomic charges of glucose-cyanohydrin

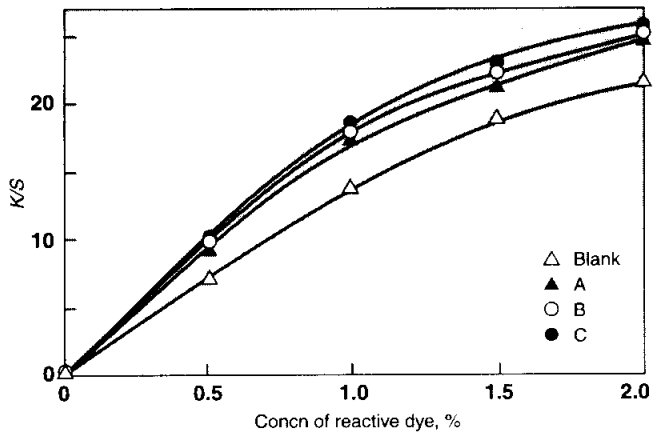


Figure 2 *K/S* values (measured at 600 nm) as a function of concentration of CI Reactive Red 2 on blank and treated wool samples, before and after extraction by a DMF/water mixture; for key see Table 1

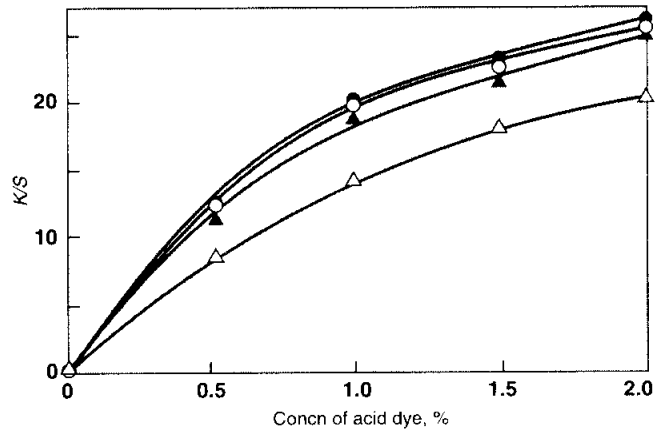


Figure 3 *K/S* values (measured at 500 nm) as a function of concentration of CI Acid Red 118 on blank and treated wool samples, before and after extraction by a DMF/water mixture; for key see Table 1

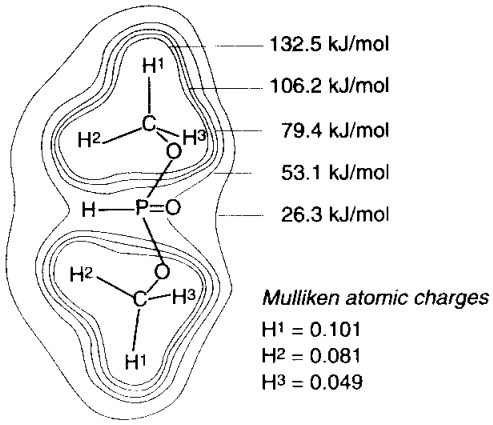
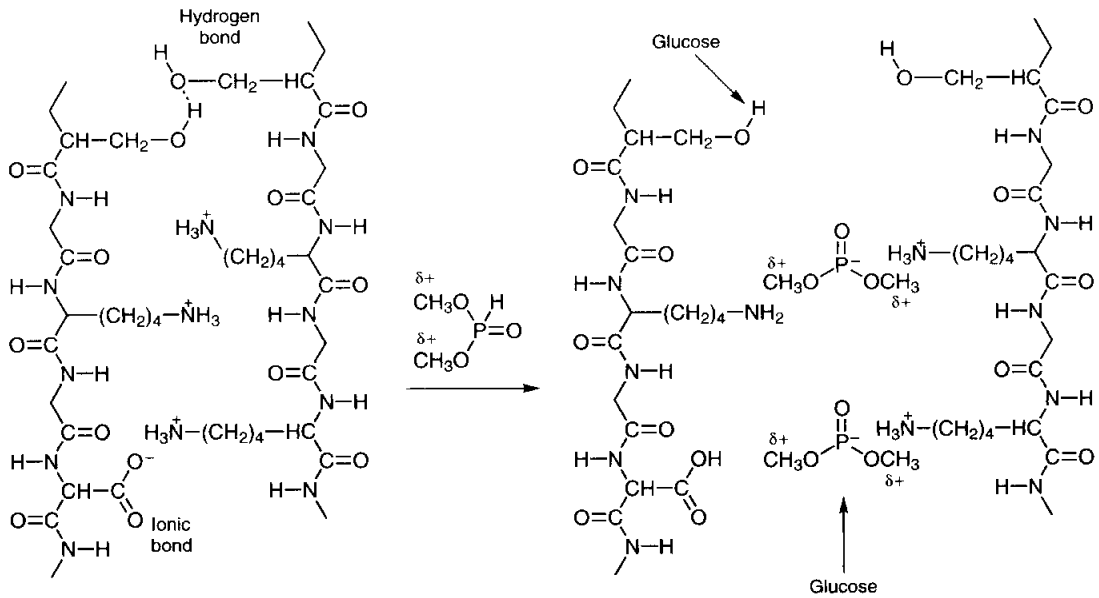


Figure 4 Calculated Mulliken atomic charges and molecular electrostatic potential map of dimethyl phosphite in the plane determined by the three hydrogens of the methoxy group

charge and the hydroxyl group connected to it acts as a leaving group. Therefore the reaction occurs at a considerably lower temperature (40°C) and within a shorter time (20 min).

The modified Strecker (P-Mannich) reaction, conducted for 30 min at 80°C, was verified by the data of Table 1 and Figures 2 and 3. This reaction proved to be the most effective in generating fibre swelling and in increasing dye pick-up. Hence it can be assumed that the dimethyl phosphite helps to open up the structure of wool in the course of treatment.

On the basis of this assumption, pretreatments were carried out with dimethyl phosphite alone. Subsequent dyeing confirmed the role of dimethyl phosphite alone in increasing dye pick-up, although to a lesser extent than in simultaneous application with glucose. The effect experienced was interpreted by quantum chemical calculations



Scheme 5

to be based on the charge distribution in dimethyl phosphite (Figure 4). Positive charge is thought to be delocalised around the hydrogens of the methoxy groups, making the compound able to eliminate structural water. Another effect of this compound is in breaking salt linkages (ionic bonds) in wool, in a similar way to the action of some quaternary bases.

Thus with the modified Strecker reaction a multiple effect has to be considered:

(a) Penetration of dimethyl phosphite into the fibre, accompanied by decomposition of salt linkages and elimination of structural water in a multi-step hydration process; new salt linkages are formed between cationic basic groups of wool protein and anionic dimethyl phosphite (Scheme 5)
(b) Penetration of glucose molecules into the opened up structure, causing further increase in accessibility of the reactive sites
(c) Formation of covalent bonds between dimethyl phosphite, glucose and amino or guanidine groups, stabilising the loosened structure.

CONCLUSION

The application of new keratin chemical reactions (Maillard, Strecker, modified Strecker) has succeeded in achieving considerable increase in dye pick-up, in both acid and reactive dyeing. Pretreatments caused slight fibre swelling without deterioration of the physico-mechanical properties or secondary structure of wool. The pretreatment reagents opened up the rather dense structure of wool, enabling easier access to its functional groups by dye molecules.

The pretreatments described offer practical and economic benefits in wool dyeing. Uniform and deep shades of good fastness characteristics can be achieved at low temperatures and with shorter dyeing procedures. Improved exhaustion enables better utilisation of the dyebath. The efficiency of the modified Strecker reaction proved to be slightly better than that of the other two pretreatments.

* * *

The authors express their thanks to the Hungarian National Scientific Research Fund (OTKA grant T0015597) for the financial support of the present work.

REFERENCES

1. L Trézl *et al.*, *Melliand Textilber.*, **74** (1993) 775.
2. L Trézl *et al.*, *J.S.D.C.*, **111** (1995) 293.
3. P R Brady and J A Rippon, *J.S.D.C.*, **108** (1992) 114.
4. *Wool dyeing*, Ed. D M Lewis (Bradford: SDC, 1992).
5. V Horváth *et al.*, *Periodica Polytechnica Ser. Chem. Eng.*, **36** (3) (1992) 209.
6. L Trézl *et al.* in *Maillard reactions in chemistry, food and health*, Ed. T P Labuza *et al.*, (Cambridge: RSC, 1994) 364.
7. A Strecker, *Ann. Chem.*, **75** (1850) 27.
8. H Kiliani, *Ber.*, **13** (1885) 3066.
9. T Hideyo *et al.*, *J. Synth. Org. Chem.*, **8** (1994) 763.
10. J B Caldwell, S J Leach and B Milligan, *Text. Res. J.*, **36** (1966) 1091.
11. P Kubelka and F Munk, *Z. Tech. Phys.*, **12** (1931) 593.