Chemistry of Natural Compounds, Vol. 34, No. 2, 1998

CHEMICAL TRANSFORMATIONS IN THE CHAINS OF CELLULOSE DIALDEHYDES AND CELLULOSE ETHERS

A. A. Sarymsakova, Sh. Nadzhimutdinov, and Yu. T. Tashpulatov

541.6.69:615.01

Nucleophilic exchange reactions of cellulose dialdehydes and ethers with a series of nucleophilic reagents have been investigated and the structural features of the reaction products have been established.

Among the products of the selective oxidation of cellulose, a great role is played by its carbonyl derivatives, especially the dialdehyde derivatives.

Dialdehydecellulose (DAC) is a complex intermediate polymer characterized by a multiplicity of possible chemical transformations, to the study of which a large number of investigations have been devoted. For an explanation of its individual reactions and properties, several chemical structures have been proposed for it, each of which explains one property but contradicts others. The structure proposed in [1] most fully reflects all the properties of DAC and can be used successfully to explain the properties of dialdehydes of cellulose ethers (DACEs).

It is known that, on periodate oxidation, partially substituted cellulose ethers form dialdehyde derivatives. The number of dialdehyde units depends on the degree of substitution of the ether, the method by which it was produced, and the uniformity of the distribution of ether groups along the ether macromolecule and between the hydroxy groups of the elementary cellulose unit [2].

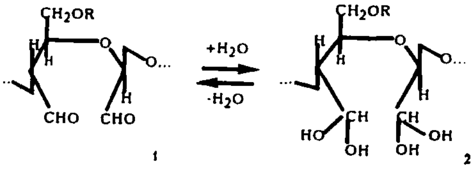
As compared with DAC, DACEs are even more complicated systems the numerous possible transformations of which have scarcely been investigated. A systematic investigation of the differences in the reactivities of the structural forms of the carbonyl groups in the dialdehyde units of DAC and DACEs and of the influence of the substituent on the electrophilicity of the aldehyde groups in DACEs was therefore of interest.

As reagents we used a number of compounds with groups differing in chemical structure and degree of nucleophilicity. The reaction products were identified on the basis of their solubilities and the results of elementary analysis and of IR and UV spectrometry.

We investigated samples of sodium-periodate-oxidized methylcellulose, hydroxyethylcellullose, carboxymethylcellulose, and triphenylmethylcellulose with various degrees of etherification and oxidation.

We have shown previously that in the periodate oxidation of cellulose the glucopyranose ring is irreversibly disrupted with the production of a dialdehyde link in the form of three types of structures that exist in dynamic equilibrium with one another [1]. We have also established that, in the periodate oxidation of cellulose ethers, units not bearing ether substituents and 6-O-monosubstituted glucopyranose rings undergo oxidation. Other variants of substitutions of ether groups are not affected by the oxidant.

Thus, on the periodate oxidation of cellulose ethers the number of structural forms of their dialdehydes increases and new structural forms appear: 6-O-substituted dialdehydes (1) and their hydrated structures (2):



1 2

R= $-CH_2COONa$; $-CH_3$; $-CH_2$-CH_2-OH; $-C$-(C_6H_5).

Institute of the Chemistry and Physics of Polymers, Academy of Sciences of the Republic of Uzbekistan, fax (3712) 44 26 61. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 212-217, March-April, 1998. Original article submitted February 24, 1997.

TABLE 1. Limiting Nucleophilic Substitution of DAC and DACEs with INAH and Hydroxylamine

Polymer with electrophilic groups		Maximum degree of substitution			
		reaction with INAH		recondensation of the reaction product with hydroxylamine	
name	degree of oxidation, m°	N, %	N=R— base-mole	N, %	N=R— base-mole
DAC	38	6.90	35	9.93	34
DACMC	22	3.28	20	3.50	14
DACMC	30	4.84	28	6.20	16
DACMC	40	6.41	37	8.06	17.2
DATRC	42	3.64	39	3.82	3
DATRC	61	5.01	56	5.19	5
DATRCMC	16	1.04	14	1.21	1

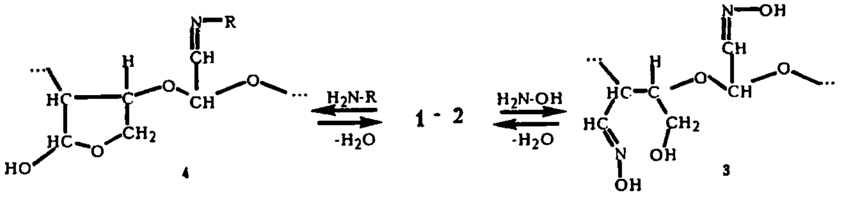
In the limiting case, when only the primary hydroxy groups in cellulose ethers are substituted, the products of their periodate oxidation consist of 6-O-substituted dialdehyde units (**1**) and their gem-diols (**2**), the equilibrium being strongly shifted in the direction of structure (**2**). This has been confirmed by the formation of a dialdehyde of triphenylmethylcellulose with a degree of etherification $\gamma = 100$, the IR spectrum of which lacked the absorption bands of the carbonyl of an aldehyde group [3].

Differences in the reactivities of the carbonyl groups in the dialdehyde units of DAC and DACEs have been considered for the exemplary case of their substitutions by nucleophilic reagents: hydroxylamine, aniline, 4-amino-3-isoxazolidone, 2-(*p*-aminobenzenesulfonamido)-5-ethyl-1,3,4-thiadiazole, isonicotinic acid hydrazide (INAH), and hydrazophthalazine [sic; hydrazino- ?], which have different pK_b values. By analogy with the reactions of DAC, it may be assumed that the direction of the reaction (each of the structural forms reacts) and the chemical structures of the reaction products must depend both on the structure of the matrix and on the nucleophilicity of the reagent.

We determined the limiting values of the degree of substitution of the DACEs and their dependence on the pH of the aqueous solution. It was established that, depending on the nature of the radical R, each nucleophilic reagent with an NH_2 group had its own conversion maximum with one and the same dialdehyde in a medium with a definite pH value.

If it is considered that the lower the nucleophilicity of the reagent the greater the amount of acid required for the catalytic reaction of aldehydes with compounds of the type of RN_2 [4], the nucleophilicities of the above-mentioned compounds rise in the sequence INAH < 4-amino-3-isoxazolidone 2-(*p*-aminobenzenesulfamido)-5-ethyl-1,3,4-thiadiazole < hydrazophthalazine [sic; hydrazino- ?] < aniline < hydroxylamine.

The great nucleophilicity of hydroxylamine ($pK_b = 5.88$) is explained by the fact that, in contrast to the others, it also reacts with the hemiacetal form of the aldehyde groups of the dialdehyde of CMC (DACMC). This was shown by a determination of the limiting value of the degree of substitution — for each oxidized glucopyranose ring two molecules of hydroxylamine are consumed with the formation of (**3**), while one molecule of each of the other nucleophilic reagents is consumed with the formation of structure (**4**):



We then attempted to introduce a molecule of the nucleophilic reagent INAH ($pK_b = 10.19$) into an oxidized glucopyranose ring and DACMC.

Investigations of the reaction of DACMC with INAH showed that changes in the reaction parameters did not lead to an increase in the amount of INAH in the polymer to more than 50% of the total number of aldehyde groups. Similar results have been obtained previously in the reaction of DAC with phenylhydrazine [5-8]. The authors of these papers consider that one of the aldehyde groups is involved in a cyclic hemiacetal and the second is free and capable of taking part in a reaction with phenylhydrazine.

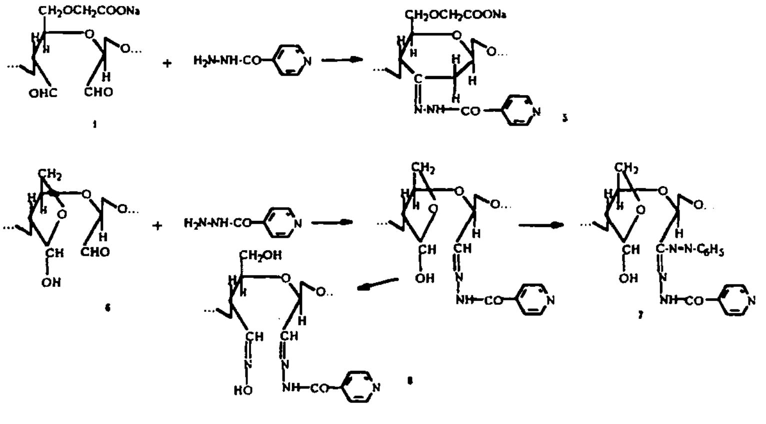
TABLE 2. Dependence of the Maximum Conversion of DAC and DACEs on the Number of Dialdehyde groups (m°) and the Reaction Medium (molar ratio of electrophil to nucleophil, 1:2)

Compound*	Degree of oxidation, m°	In an alcoholic medium		In an aqueous medium	
		N, %	N=R-base-mole, %	N, %	N=R-base-mole, %
Aniline					
Cellulose	38	2.42	32	2.20	29
CMC γ=70	27	1.63	25	1.47	24
MC γ=160	20	1.17	18	1.05	16
HEC γ=180	27	1.17	18	1.05	16
TRC γ=104	27	1.54	24	1.30	20
Hydroxylamine					
Cellulose	38	6.20	79	6.27	79
CMC	27	2.98	55	2.94	55
MC	20	2.35	37	2.29	36
HEC	20	2.40	39	2.34	38
TRC	20	1.54	39	1.34	38
Isonicotinic acid hydrazide					
Cellulose	20	4.24	20	3.98	18
CMC	24	2.76	18	2.98	22
MC	18	2.14	14	2.21	16
HEC	20	2.87	20	2.64	18
TRC	27	1.97	25	1.71	22
2-(*p*-Aminobenzenesulfonamido-5-ethyl-1,3,4-thiadiazole					
CMC	18	4.05	16	3.61	13
MC	16	3.81	14	2.96	11
1-Hydrazophthalazine					
Cellulose	40	–	–	7.99	31
CMC	22	–	–	4.43	18
MC	18	–	–	3.48	14
4-Amino-3-isoxazolidin-3-one					
Cellulose	20	–	–	3.07	19
CMC	18	–	–	2.76	18
MC	27	–	–	1.58	24

Note. MC) methylcellulose; HEC) hydroxyethylcellulose; TRC) tritylcellulose.

To elucidate the nature of the second aldehyde group, the dialdehyde of triphenylmethylcellulose, in which the possibility of the formation of a hemiacetal bond is excluded (since all the hydroxy groups at C_6 are substituted), was condensed with tolylhydrazine. The authors succeeded in changing the direction of the condensation of the dialdehyde of triphenylmethylcellulose with tolylhydrazine in the direction of the restoration of the C_2-C_3 bond of the glucose ring with the formation of a compound containing an arylazo group at the third carbon atom [9], which did not react with benzenediazonium.

Apparently, in DACMC the majority of the oxidized units have a protective group (in this case, carboxymethyl) at C_6, like the dialdehyde of triphenylmethylcellulose, and on condensation with INAH the open ring of the CMC dialdehyde is restored with the formation of an arylazo group. To confirm this, we treated the reaction products with biphenyldiazonium chloride. The absence of a formazan group from the reaction product showed that, apparently, on the condensation of CMC dialdehyde with INAH, in the units with a carboxymethyl group at C_6 the reaction took place with the restoration of the ring:



This may explain the fact that, in contrast to DACMC, treatment with benzenediazonium chloride of the product of the condensation of DAC with INAH led to compound (7), containing a formazan grouping.

The second aldehyde group involved in a cyclic acetal in the product of the condensation of DAC and INAH was identified directly by its reaction with hydroxylamine (compound (**8**)).

It is known that, because of its high nucleophilicity, hydroxylamine reacts with both aldehyde groups of the oxidized glucopyranose ring of DAC [9]. Therefore, in the condensation with hydroxylamine of the product of the reaction of DAC with isonicotinic acid hydrazide the aldehyde group involved in the cyclic hemiacetal undergoes condensation with the formation of structure (**8**).

As can be seen from Table 1, a second condensation with hydroxylamine of the product of the reaction DAC+INAH led to the addition of one hydroxylamine molecule to each glucopyranose ring. In the case of CMC dialdehyde, however, the amount of added hydroxylamine was less than that corresponding to the total number of oxidized units. This is explained by the fact that, on periodate oxidation, not only the unsubstituted glucopyranose rings but also the 6-O-substituted carboxymethyl units, the opening of rings of which was restored on their condensation with INAH, underwent oxidation. To confirm this hypothesis we investigated the condensation of 6-O-triphenylmethyl-2,3-dialdehydecellulose (DATRC) and 6-O-carboxymethyl-6-O-triphenylmethyl-2,3-dialdehydecellulose (DATRCMC) with INAH.

The product of the reaction of DAC with INAH was subjected to recondensation with hydroxylamine. As can be seen from Table 1, the reaction products contained practically no added hydroxylamine, which confirmed the reality of the formation of structure (5).

Thus, the absence of a compound with a formazan group in the products of the condensation of DATRC and DATRCMC with INAH on their subsequent treatment with biphenyldiazonium chloride and the presence of one molecule of INAH in each oxidized glucopyranose ring, and also the impossibility of introducing hydroxylamine molecules into the same units, confirmed that when DAC having a protective group at C_6 is condensed with INAH the reaction takes place with restoration of the opened glucopyranose rings of aryl compounds of type (5).

On the basis of the results of investigations of the condensation of DAC and DACEs with the nucleophilic reagents listed above, conditions were found for their maximum conversion, and these are given in Table 2.

Thus, it has been established that on the interaction of DAC and DACEs with a number of nucleophilic reagents the degree of conversion is determined by the nature of the ether substituents in the cellulose derivatives and by the pK_b value of the nucleophilic reagent.

EXPERIMENTAL

The periodate oxidation of cellulose and its ethers was achieved by a method that we have described previously [1]. It was carried out at pH 4.7 in a 3% aqueous solution of the cellulose ether at an oxidant concentration of 0.5 M and a temperature of 25°C for 2.5 h. The yield of oxidation product amounted to from 60 to 72%, depending on the composition of the initial cellulose ether. The degree of oxidation of the product in each case was determined by the iodometric method [10] and UV-spectroscopically from the consumption of IO_4^- ions, as shown by the change in the intensity of the absorption band at $\lambda = 222$ nm.

The maximum substitution of DAC and DACEs with nucleophilic reagents was achieved in a thermostated three-necked flask fitted with a thermometer and stirrer. The flask was charged with 0.02 mole of DAC or a DACE and 40 ml of an alcoholic or aqueous solution containing 0.06 mole of the nucleophilic reagent, and the mixture was stirred vigorously at 25°C for 1 h. Then the reaction product was filtered off, washed repeatedly with a mixture of alcohol and water (1:1), and dried over P_2O_5 in a desiccator.

Degrees of substitution were determined from the nitrogen contents of the reaction products.

REFERENCES

1. Sh. Nadzhimutdinov, A. A. Sarymsakov, and Kh. U. Usmanov, Cellul. Chem. Technol., **9**, No. 6, 617 (1975).
2. Sh. Nadzhimutdinov, A. A. Sarymsakov, and Kh. U. Usmanov, Cellul. Chem. Technol., **15**, No. 6, 613 (1981).
3. I. N. Ermolenko, Spectroscopy in the Chemistry of Oxidized Celluloses [in Russian], Minsk (1959), p. 164.

4. H. Becker, in: Modern Problems of Physical Organic Chemistry [Russian translation], IL, Moscow (1967), p. 250.
5. G. Rakhmanberdiev, Sh. Mirnigmatova, T. G. Gafurov, and Kh. U. Usmanov, Dokl. Akad. Nauk Uz., No. 6, 36 (1970).
6. W. C. Barry and P. W. Mitchell, J. Chem. Soc., 4020 (1954).
7. W. C. Barry, J. E. McCormic, and P. W. D. Mitchell, J. Chem. Soc., 3692 (1954).
8. L. Mester, J. Am. Chem. Soc., **77**, 5452 (1955).
9. Yu. S. Kozlova and Z. A. Rogovin, Vysokomol. Soedin., **2**, 614 (1960).
10. A. B. Pakshver (ed.), Handbook on Analytical Control in the Production of Synthetic and Artificial Fibers [in Russian], Moscow (1957), p. 271.