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STUDY OF HEAT EFFECTS IN TOPOCHEMICAL PROCESSES OF CELLULOSE ESTERIFICATION

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In this research, the heat effects of topochemical esterification of cellulose, namely, nitration and acetylation, were studied. Depending on the conditions, the esterification process can occur in two main topochemical directions such as bulk and local. In bulk process the reagent quickly penetrates in amorphous domains (ADs), and more slowly in crystallites (CRs) of cellulose. In local esterification, the reagent penetrates the most accessible ADs only, whereas CRs remain almost unreacted. It was found that the reaction of bulk nitration of cellulose up to a substitution degree (DS) of 1.5 is endothermic and determined primarily by the contribution of the temperature-entropy component to the negative Gibbs potential. However, if DS > 1.5, the bulk nitration becomes exothermic, and therefore, the feasibility of this process is determined by the impact of enthalpy on the negative Gibbs potential. Unlike nitration, the bulk acetylation of cellulose is always an exothermic process, regardless of the achieved degree of substitution, and this process can be implemented due to the predominant contribution of reaction enthalpy to negative Gibbs potential. In the case of local esterification of ADs, the main contribution to the negative Gibbs potential is made by the reaction enthalpy that determines the reaction feasibility. Besides, the local acetylation is more exothermic than the local nitration process.

Keywords: cellulose esterification, topochemistry, bulk esterification, local esterification, standard enthalpy of formation, reaction enthalpy.

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Introduction

Among diverse cellulose derivatives, two esters, nitrates, and acetates of cellulose are the most widespread and have practical importance. Nitrocelluloses are used for the production of plastics, membranes, films, protective coatings, adhesives, paints, varnishes and enamels, powders, rocket fuels, explosives, etc. [1]. It was shown that the application area of use depends on the degree of substitution (DS) of the nitrocellulose (NC) sample [2]. If DS is less than 1.5, this type of NC can only be used to produce paints, varnishes, and enamels. NC having DS between 1.5 and 2.4 is used for the production of plastics and membranes. If DS > 2.4, then this type of NC can be used to produce smokeless powder, rocket propellants, and explosives.

For their part, cellulose acetate called also acetylcellulose (AC) with various DS is used in the production of hydrophobic fillers, and reinforcements compatible with hydrophobic polymers, as well as in the compositions of hydrophobic coatings, paints, adhesives, and other hydrophobic materials [3–6]. Moreover, these cellulose esters are applied in the technology of thermoplastics, electronic device housings, spectacle frames, anti-fog goggles, cigarette filters, semi-permeable and separating membranes, optical films, heat, and rot-resistant fabrics, self-cleaning materials, protective coatings, and other materials.

It is known that depending on the conditions, the cellulose esterification can proceed in two main topochemical directions such as bulk and local.

In bulk process, the reagent quickly penetrates in amorphous domains (ADs), and more slowly in crystallites (CRs) of cellulose, resulting in cellulose decrystallization and the formation of an ester with amorphized structure [7–11]. The cellulose crystallinity affects the rate of esterification reaction but has little impact on the final degree of substitution.

The cellulose can be bulk nitrated with concentrated nitric acid alone or with various nitrating systems, such as mixtures of nitric acid, sulfuric acid, and water; nitric acid, phosphoric acid, and phosphoric anhydride; nitric acid, acetic acid, and acetic anhydride; nitric acid and its salts; nitric acid and dichloromethane; nitric acid and ether; etc. [2, 12]. However, for the industrial production of NC, only mixtures of nitric with sulfuric acid and water are used. The cellulose nitration can be carried out at temperatures of 273–313 K for 30–60 min, at a ratio of the nitrating system to cellulose 30–50. The DS value of the resulting NC is adjusted by changing the composition of the reaction mixture, especially the water content.

In the bulk acetylation, the starting cellulose material is activated and then placed in a suitable organic liquid (e.g., acetic acid, methylene chloride, etc.) and then treated with acetic anhydride in the presence of a small amount of catalyst, usually sulfuric or perchloric acid [13]. The reaction is performed at temperatures of 303 to 313 K for 60 min, at a ratio of the acetylating system to cellulose 10–20. As a result of bulk esterification, cellulose triacetate (TAC) is usually produced. To obtain an ester with a lesser degree of substitution, additional acid treatment of the primary TAC is carried out.

The second topochemical direction is the local esterification of only the most accessible cellulose ADs, while CRs remain almost unreacted. This local nitration process is observed if the nitrating mixtures contain an increased amount of water. On the other hand, local acetylation can be achieved by treating cellulose with vapors of acetic anhydride.

Although the chemical aspects of cellulose esterification are well known, its thermochemistry is largely unexplored. It is only found that the processes of bulk esterification can be exothermic. However, the heat effects of local esterification have been not studied. This article is devoted to solving this problem.

Materials and methods

Materials. The original cellulose material was pure cotton cellulose, CC (98% α-cellulose, DP=2700) supplied from Hercules, Inc., USA. Amorphous cellulose (AM) was prepared by ball-milling of CC with ceramic balls for 10 h. The needed chemicals were acquired from Sigma-Aldrich Co.

Methods.

Esterification of cellulose. The bulk nitration of CC was carried out at 293 K with a liquid reagent system-to-cellulose ratio of 50 for 60 min using mixtures of nitric acid, sulfuric acid, and water. To achieve the DS=0.97, the reagent system contained 25 wt.% HNO_3, 49 wt.% of H_2SO_4 and 26 wt.% H_2O. To obtain DS=2.03, the reagent system contained 28 wt.% HNO_3, 53 wt.% of H_2SO_4 and 19 wt.% H_2O. NC with DS=2.85 was synthesized using the reagent system containing 36 wt.% HNO_3, 60 wt.% of H_2SO_4 and 4 wt.% H_2O. The obtained NC samples were washed with cold water and 1% NaHCO3 to a neutral pH value; then the samples were washed with hot water (358 K), cold water, rinsed with anhydrous methanol, and dried in a vacuum chamber at 323 K to constant weight.

The bulk acetylation of the initial cotton cellulose (CC) was carried out by acetic anhydride (AcAn) in the medium of trifluoroacetic acid at 323 K for 1 h using a liquid reagent system-to-cellulose ratio of 50 [14]. The degree of substitution of obtained AC samples was adjusted by a change in the molar ratio of AcAn to cellulose. Finally, the obtained AC samples were washed with water, rinsed with anhydrous ethanol, and dried in a vacuum chamber at 323 K to constant weight.

Characterization of samples. The substitution degrees of cellulose esters were determined using conventional methods of chemical analysis [13]. The DS values of nitrocellulose samples were calculated from nitrogen percentage (N %):

$$SD = 3.6\ N/(31.1 - N) \quad (1)$$

For acetylcellulose samples, DS values were calculated using the percentage of acetyl groups (AcG %):

$$DS = 3.86\ AcG/(102.4 - AcG) \quad (2)$$

Enthalpy of interaction with water. The standard enthalpies of the interaction of the dry cellulose samples with water, i.e., wetting enthalpies ($\Delta_w H$), were measured at 298 K using a TAM Precision Solution Calorimeter [15]. The released exothermic heat effect was measured with accuracy ±0.01 J. Three of the same samples were tested to calculate a reliable enthalpy value and standard deviation.

The degrees of crystallinity (X) and amorphicity (Y) of cellulose were calculated as follows:

$$X = 1 - (\Delta_w H/\Delta_w H_{am}) \tag{3}$$

$$Y = 1 - X \tag{4}$$

where $\Delta_w H_{am} = -27.2$ kJ/mol is the standard wetting enthalpy of completely amorphous cellulose (AC).

Enthalpies of combustion and formation. Combustion of the dry samples was carried out in a stainless-steel calorimetric bomb having a volume of 0.320 dm^3 at an oxygen pressure of 3.05 MPa with 1.00 cm^3 of deionized water added to the bomb [14]. The combustion measurements were carried out by an isothermal water calorimeter at 298.15 K with an accuracy of ±0.001 K. To adjust the enthalpy of combustion (ΔH_c) to standard conditions the Washburn correction, as well as the correction for the change in the number of moles of gases before and after combustion was introduced. For each sample, five experiments were performed to calculate the reliable value of combustion enthalpy and standard deviation.

The standard enthalpy of formation ($\Delta_f H$) of one mole of the repeating unit of cellulose and cellulose esters having formulas $C_aH_bO_c$ and $C_aH_bO_cN_d$ can be calculated from the measured standard enthalpy of combustion ($\Delta_c H$) using the known equation:

$$\Delta_f H = a\, \Delta_f H(CO_{2,\,g}) + 0.5b\, \Delta_f H\, (H_2O,_{l}) - \Delta_c H \tag{5}$$

where $\Delta_f H(CO_{2,\,g}) = -393.51$ kJ/mol and $\Delta_f H(H_2O,_{l}) = -285.83$ kJ/mol are standard enthalpies of the formation of carbon dioxide and liquid water, respectively.

Results and discussion

Thermodynamic characteristics of samples

The thermodynamic (TD) characteristics of studied cellulose samples and cellulose esters are presented in Table 1. From the linear dependences of TD functions on DS, the TD characteristics of mono-, sesqui-di-, and tri-substituted esters were also calculated using the following equations.

For nitrocelluloses:

$$\Delta_c H \text{ (kJ/mol)} = -2845.1 + 45.7 \text{ DS} \tag{6}$$

$$\Delta_f H \text{ (kJ/mol)} = -945.1 + 96.8 \text{ DS} \tag{7}$$

For acetylcelluloses:

$$\Delta_c H \text{ (kJ/mol)} = -2845.1 - 890.1 \text{ DS} \tag{8}$$

$$\Delta_f H \text{ (kJ/mol)} = -945.1 - 185.0 \text{ DS} \tag{9}$$

For comparison with the TD characteristics obtained in this study, some literature data were presented in Table 2, and Figures 1, 2. As can be seen, the obtained results are confirmed by literature data.

For TD calculations of cellulose esterification, the literature data on standard formation enthalpies of the reagents and low-molecular-weight products of esterification were also used (Table 3).

The obtained TD characteristics were used for thermochemical analysis of bulk and local esterification of cellulose to different DS values.

Bulk esterification

The bulk process is accompanied by decrystallization (melting) of cellulose crystallites and esterification of amorphized cellulose (AM) with the formation of amorphous esters. This process can be described by the following TD equations:

$$\Delta_r H(CC) = \Delta_r H(AM) + X\,\Delta_m H \tag{10}$$

where $\Delta_r H(CC)$ and $\Delta_r H(AM)$ are enthalpies of bulk esterification of cotton cellulose (CC) and amorphized cellulose (AM), respectively; $\Delta_m H=35.1$ (kJ/mol) is the melting enthalpy of CI crystallites, while X=0.7 is the crystallinity degree of CC sample.

Table 1. Standard TD characteristics of studied samples

Sample	SD	$-\Delta_c H$, kJ/mol	$-\Delta_f H$, kJ/mol
*CR	0	2810.0	980.2
CC	0	2821.2	969.0
AM	0	2845.1	945.1
NC-1	0.97	2800.8	851.2
NC-2	2.03	2752.3	748.6
NC-3	2.85	2714.8	669.2
NC-4	0.62	2817.0	885.1
MNC	1	2799.4	848.3
SNC	1.5	2776.6	799.9
DNC	2	2753.7	751.5
TNC	3	2708.0	654.7
AC-1	1.11	3933.0	1150.3
AC-2	2.12	4731.8	1337.2
AC-3	2.80	5337.2	1463.4
MAC	1	3735.1	1130.1
SAC	1.5	4180.3	1223.0
DAC	2	4625.2	1315.3
TAC	3	5515.4	1500.2

*Note: data for CI crystallites (CR) were taken from [16].

The melting enthalpy of CI crystallites is $\Delta_m H = \Delta_f H\ (AM) - \Delta_f H\ (CR) = 35.1$ (kJ/mol)

Table 2. Standard TD characteristics of samples

Sample	$-\Delta_c H$, kJ/mol	$-\Delta_f H$, kJ/mol	Reference
Cotton linter	2824.1	966.1	[17]
Amorphized cellulose	2842.8	947.4	[18]
	2845.3	945.0	[19]
	2847.8	942.4	[16]
NC, DS=2.12	2748.2	742.7	[17]
DNC	2751.6	753.3	[17]
TNC	2709.4	653.0	[17]
AC, DS=1.60	4263.5	1243.3	[20]
AC, DS= 2.36	4890.2	1431.9	[20]
AC. DS=2.83	5316.1	1510.0	[20]

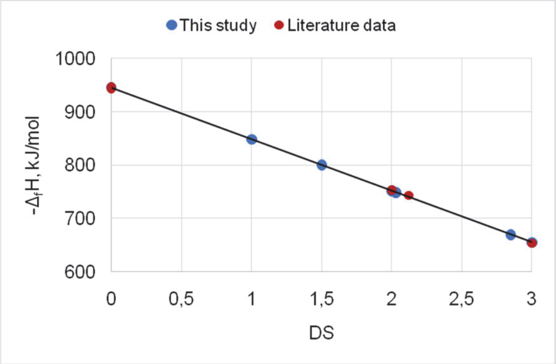

Fig. 1. Dependence of standard formation enthalpy on the degree of substitution of NC samples

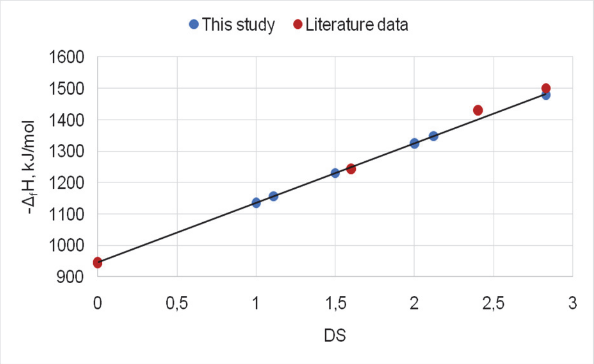

Fig. 2. Dependence of standard formation enthalpy on the degree of substitution of AC samples

Table 3. The standard formation enthalpies of substances

Liquid Substance	Symbol	$-\Delta_f H$, kJ/mol
Nitric Acid	HNO_3	173
Acetic Anhydride	AcAn	625
Acetic Acid	AcAc	484.5
Water	H_2O	285.83

The enthalpy of bulk nitration of AM in eq. (10) can be expressed, as follows:

$$\Delta_r H(AM) = \Delta_f H(NC) + DS\,[\Delta_f H(H_2O) - \Delta_f H(HNO_3)] - \Delta_f H(AM) \tag{11}$$

And the enthalpy of bulk acetylation of AM was also calculated:

$$\Delta_r H(AM) = \Delta_f H(AC) + DS\,[\Delta_f H(AcAc) - \Delta_f H(AcAn)] - \Delta_f H(AM) \tag{12}$$

The formation enthalpies of AM, NC, and AC samples with various DS, as well as reagents (HNO_3 and AcAn) and low-molecular-weight products of esterification (H_2O and AcAc), are presented in Tables 1 and 3.

The resulting enthalpies of bulk esterification of cotton cellulose are shown in Tables 4 and 5, while the dependences of these TD functions on DS can be seen in Figure 3.

As can be seen from Table 4, the reaction of bulk nitration of cellulose up to SD of 1.5 is endothermic, and therefore its implementation requires an influx of thermal energy from the outside. However, it is known that bulk nitration of the cellulose also proceeds when the reaction system is cooled to relatively low temperatures when the supply of thermal energy from the outside is difficult [21]. In this case, the only possibility for the nitration reaction is to increase the temperature-entropy component so that the Gibbs potential of this reaction becomes negative, namely:

$$T\,\Delta S_r > \Delta H_r \text{ and } \Delta G_r = (\Delta H_r - T\,\Delta S_r) < 0 \tag{13}$$

where ΔG_r is the standard Gibbs potential of the reaction, and T is temperature.

Thermodynamic analysis shows that the process of bulk nitration of cellulose with a dilute nitrating mixture to SD below 1.5 can only be implemented if the positive temperature-entropy component contributes to the Gibbs potential. On the other hand, when cellulose is nitrated with more concentrated nitrating mixtures to SD>1.5, the reaction enthalpy becomes exothermic. Thus, when the bulk nitration of cellulose is carried out to increased DS values, the feasibility of this reaction is determined mainly by the contribution of enthalpy to the negative Gibbs potential.

Unlike nitration, the bulk acetylation of cellulose is always an exothermic process, regardless of the achieved DS value (Table 5). Moreover, the more SD, the higher the exothermic heat effect of this reaction. It can be also noted that an increase in reaction entropy and temperature-entropy component will facilitate the implementation of the acetylation process. However, if the reaction entropy decreases, then the following conditions must be fulfilled for the implementation of bulk acetylation of cellulose:

$$[\Delta H_r] > [T\,\Delta S_r] \text{ and } \Delta G_r = (\Delta H_r - T\,\Delta S_r) < 0 \tag{14}$$

Anyway, the feasibility of bulk acetylation is determined mainly by the exothermic enthalpy of this reaction.

The results also showed that bulk acetylation is accompanied by the release of significantly more heat energy than in the case of bulk nitration (Fig. 3).

Table 4. Enthalpies of bulk nitration reaction of CC

NC *(B)	DS	$\Delta_r H$, kJ/mol
MNC (B}	1	8.6
SNC (B)	1.5	0.6
DNC (B)	2	-7.5
TNC (B)	3	-23.5

*Symbol (B) denotes the bulk reaction

Table 5. Enthalpies of bulk acetylation reaction of CC

AC *(B)	DS	Δ_rH, kJ/mol
MAC (B}	1	-19.8
SAC (B)	1.5	-42.9
DAC (B)	2	-64.6
TAC (B)	3	-112

*Symbol (B) denotes the bulk reaction

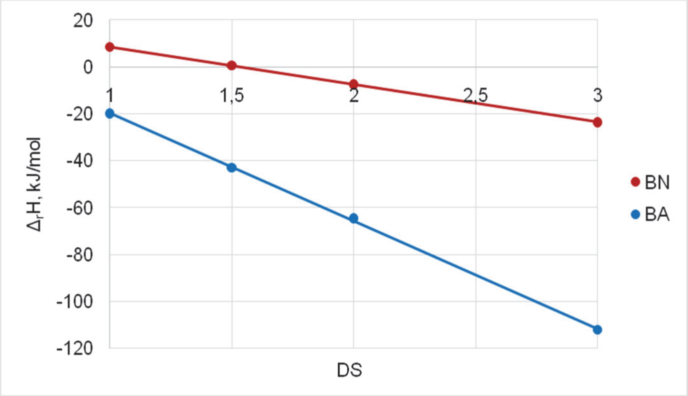

Fig. 3. Dependence of reaction enthalpy on the degree of substitution for bulk nitration (BN) and bulk acetylation (BA) of cotton cellulose

Local esterification

Consider the local esterification of only the most accessible amorphous domains of cellulose when the crystalline regions (CR) of the sample remain unreacted. The process of such local reactions, nitration and acetylation, can be described, as follows:

$$CC + Y\ DS_a\ HNO_3 \rightarrow Y\ NC + Y\ DS_a\ H_2O + X\ CR \qquad (15)$$

$$CC + Y\ DS_a\ AcAn \rightarrow Y\ AC + Y\ DS_a\ AcAc + X\ CR \qquad (16)$$

where Y=0.3 is the amorphicity degree, X=0.7 is the crystallinity degree of CC, and DS_a is the degree of substitution of AD.

Then, the enthalpy for the reactions of local esterification of CC was calculated using the following equations:

$$\Delta_rH(CC) = X\ \Delta_fH(CR) + Y\ \Delta_fH(NC) + Y\ DS_a\ [\Delta_fH(H_2O) - \Delta_fH(HNO_3)] - \Delta_fH(CC) \qquad (17)$$

$$\Delta_rH(CC) = X\ \Delta_fH(CR) + Y\ \Delta_fH(AC) + Y\ DS_a\ [\Delta_fH(AcAc) - \Delta_fH(AcAn)] - \Delta_fH(CC) \qquad (18)$$

The obtained results are shown in Tables 6, 7, and Figure 4.

Table 6. Enthalpies of local nitration reaction of CC

NC *(L)	DS	Δ_rH, kJ/mol
MNC (L}	1	-5.3
SNC (L)	1.5	-7.6
DNC (L)	2	-10.5
TNC (L)	3	-14.8

*Symbol (L) denotes the local reaction

Table 7. Enthalpies of local acetylation reaction of CC

AC *(L)	DS	Δ_rH, kJ/mol
MAC (L}	1	-14
SAC (L)	1.5	-20.3
DAC (L)	2	-27.4
TAC (L)	3	-40.7

*Symbol (L) denotes the local reaction

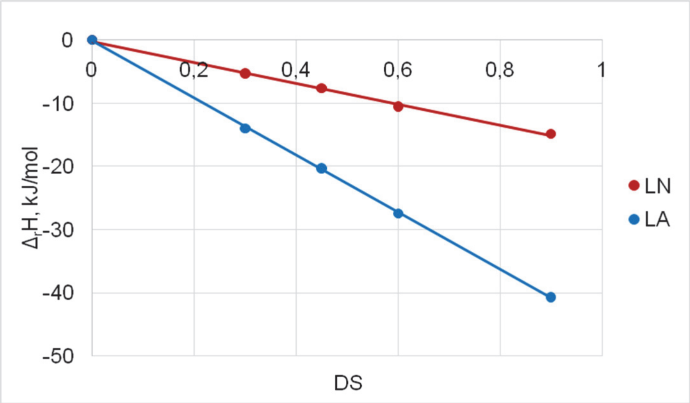

Fig. 4. Dependence of reaction enthalpy on the degree of substitution for local nitration (LN) and local acetylation (LA) of cotton cellulose

From Figure 4 it follows that local acetylation is a much more exothermic process than local nitration.

Since the local esterification is an exothermic process, then its feasibility probably is determined by the contribution of reaction enthalpy to negative Gibbs potential:

$$\Delta G_r = (\Delta H_r - T\,\Delta S_r) < 0$$

Conclusions

It was found that the reaction of bulk nitration of cellulose up to a substitution degree (DS) of 1.5 is endothermic and determined primarily by the contribution of the temperature-entropy component to the negative Gibbs potential. However, if DS is above 1.5, the bulk nitration becomes exothermic. In this case, the reaction feasibility is determined by the impact of enthalpy on the negative Gibbs potential.

Unlike nitration, the bulk acetylation of cellulose is always an exothermic process, regardless of the achieved degree of substitution. Therefore, this process can be implemented due to the contribution mainly of enthalpy to negative Gibbs potential. From the obtained results it follows that bulk acetylation is accompanied by the release of significantly more heat energy than in the case of bulk nitration.

The study of local esterification of ADs showed that the main contribution to the negative Gibbs potential is made by the reaction enthalpy, which determines the process feasibility. In addition, the local acetylation is more exothermic than the local nitration process of ADs of cellulose.

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Conflict of Interest
The author of this work declares that he has no conflicts of interest.

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