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THE THERMAL DEGRADATION OF SOME CELLULOSIC MATERIALS

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ABSTRACT

The thermal degradation of pure powdered cellulose, Iraqian cotton fibers and grained extracted cellulose from some plants in the north of Iraq is studied. It is found to be a first-order reaction with rate of degradation, *k*, ranging from 1 1 to 3.1 min^{-1}

The activation energy, E_a, the entropy change, ΔS, the enthalpy change, ΔH, and the Gibbs free energy, ΔG, are calculated by applying the rate theory of the first-order reaction The variation of these parameters is discussed in the light of the variation of degree of crystallinity or the ordering and disordering structure and the nature of the cellulosic material

INTRODUCTION

Thermogravimetric analysis (TG) is widely used as a method to investigate the thermal decomposition of polymers and to determine some kinetic parameters, e.g. rate of decomposition, *k*, order of reaction, *n*, and activation energy, E_a [1]. The values of these parameters can be of major importance in the elucidation of the mechanisms involved in polymer degradation [2] and in the estimation of the thermal stability of polymers [3]. Many authors [4] studied and discussed the qualitative and quantitative estimation of the thermal degradation of polymers.

The electrical properties of the cellulosic materials were tackled previously by Hanna and co-workers [5-10]. The thermal properties of some cellulosic materials were investigated by Shafizadeh and Bradbury [11] and by Chatterjee [12]. The present investigation aims at studying the effect of the nature of the cellulose and the degree of crystallinity on the thermal degradation of some cellulosic materials. Also, the kinetic parameters (*k* and *n*) and the thermodynamic functions such as activation energy (E_a), entropy change (ΔS), enthalpy change (ΔH) and Gibbs free energy (ΔG) for the samples were calculated.

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EXPERIMENTAL

Materials

Three types of cellulosic material were used. Pure cellulose (powder), supplied by Flaka Co., Iraqian cotton fibers and grained extracted cellulose from some plants of northern Iraq.

Preparation of the cotton samples

Fibers of Iraqian cotton were cut into small pieces and shredded. The powder thus obtained was sieved to different particle sizes ranging from 0.099 to 0.5 mm in diameter. The samples were purified and dried at 70°C under vacuum before any measurements [10].

Measurement of the degree of crystallinity

The indirect method [13] was used for determining the degree of crystallinity of the samples. This method is based on the acid hydrolysis of the cellulose sample at different time intervals.

Measurement of thermal degradation

Differential thermal analysis (DTA), the weight loss thermogram (TG) and the differential thermogram (DTG) were carried out by using a MOM Derivatograph No. 3427 from 20 to 500°C. The rate of heating was adjusted at 5°C min^{-1}.

RESULTS AND DISCUSSION

The results of the sieve analysis and the degree of crystallinity for the investigated cotton samples are shown in Table 1. The thermal profiles for

TABLE 1

Characterisation of the samples

Sample no	Nature of sample	Particle size (mm)	Degree of crystallinity
1	Powdered cellulose	0.009–0.063	
2	Iraq cotton	0.009–0.063	88.10
3	Iraq cotton	0.063–0.125	88.51
4	Iraq cotton	0.125–0.250	89.12
5	Iraq cotton	0.250–0.500	90.573
6	Iraq cotton	> 0.500	91.410
7	Extracted cellulose	Grains	

one of the samples are shown in Fig. 1. This sample, which had a particle size between 0.009 and 0.063 mm, is taken as an example for the purposes of discussion. The DTA of the Iraqi cotton sample No. 2 (Fig. 1) shows an exothermic reaction beginning at ~ 300°C and ending at ~ 400°C. This exotherm is interrupted by an endotherm centered at ~ 310°C. This endothermic peak can be attributed to the formation and evaporation of some volatile pyrolysis products; the exothermic peak is due to the carbonisation of these products [11]. The TG curve for this sample (Fig. 1) can be classified into three parts. The first part, from 25 to ~ 300°C, represents the volatile materials and/or the evaporation of some residual absorbed water. The second part starts at ~ 300°C and ends at ~ 400°C, and represents the maximum thermal degradation of the samples. The third part, ranging from ~ 400 to ~ 500°C, represents the carbonisation of the products to ash. These three parts may correspond to the three steps which were suggested by Chatterjee [12] to represent the thermal degradation of cellulose.

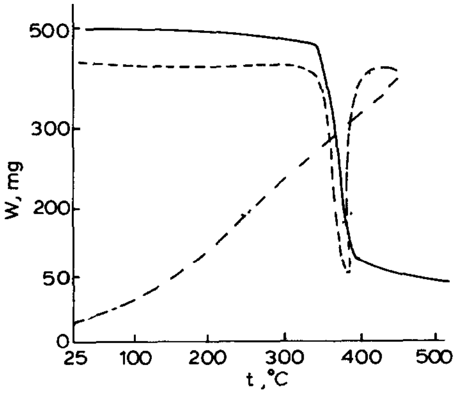

Fig. 1 Thermal analysis curves for Iraq cotton sample 2. ————, TG, - - - - - -, DTG, ·· ···, DTA; ·—·— , t°C

First step

$A \rightarrow B_1$ Initiation (volatile product)

Second step

$$\left.\begin{array}{l} B_1 \rightarrow B_2 + L \\ B_2 \rightarrow B_3 + L \\ B_n \rightarrow B_{n+1} + L \\ \Sigma B_n \rightarrow \Sigma B_{n+1} + L \end{array}\right\} \text{Propagation (thermal degradation)}$$

Third step

$\Sigma B_{n+1} \rightarrow$ carbonisation (ash) where A denotes the initial molecules of cellulose, $B_1 \ldots B_n$ are fragmented molecules, and L denotes volatile products.

The rate of degradation, k, of the samples was taken in terms of the rate of the weight loss (dW/dt). The thermal degradation of any polymer can be represented by the equation

$$\mathrm{A(solid)} \rightarrow \mathrm{B(solid)} + \mathrm{C(gas)}$$

Thus, the general rate expression may be written [14]

$$R_t = -dW/dt = (A/R_H)\, e^{-E/RT} W^n$$

where W is weight of active material remaining for a particular reaction, R_H is the rate of heating, dW/dt is the rate of degradation, A is the frequency factor, E is the activation energy, R is the gas constant, T is the temperature and n is the order of reaction. The above equation can be arranged to give

$$\ln R_t = \ln A - E_a/RT + n \ln W$$

When W is held constant, a plot of $\ln R_t$ versus $1/T$ should give a linear relation. The value of the activation energy can be calculated from the slope.

Tables 2–8 give the values of the rate constant for all samples. Figures 2 and 3 represent the variation of $\log[(W_0 - W_{500})/(W_t - W_{500})]$ against time, t min, where W_0, W_t and W_{500} are the weights of the initial sample, the sample after time t and the sample at the end of the experiment (at 500°C), respectively. The linearity of these curves indicates that the thermal degradation of all cellulosic samples is of the first order.

The activation energies of all the samples were calculated and are shown in Table 9. It is found that the values range from 56.321 to 17.847 kcal mole^{-1} depending on the nature of the sample and the degree of crystallinity. These values are in agreement with literature values [11,12,15,16].

It is frequently convenient to express the rate of reaction in terms of thermodynamic functions. According to the rate theory [17], the rate of

TABLE 2

Thermal degradation data of pure cellulose (sample 1)
$W_0 = 560$ mg; $W_{500} = 80$ mg

Time (min)	$\frac{1}{T} \times 10^5$	Weight (mg)	Loss in weight (mg)	k (min^{-1})	$\frac{W_0 - W_{500}}{W_t - W_{500}}$
0		560.000	0		
28.542	190.165	528.000	32.000	1.121	2.996
28.780	189.496	522.667	37.333	1.286	3.516
29.018	188.831	517.334	42.666	1.470	4.043
29.256	188.171	512.000	47.000	1.607	4.576
29.494	187.516	506.667	52.333	1.774	5.115
29.759	186.865	501.334	57.666	1.940	5.662

TABLE 3

Thermal degradation data of Iraqi cotton (sample 2)
Particle size = 0 009–0.063 mm; $W_0 = 500$ mg; $W_{500} = 60$ mg.

Time (min)	$\frac{1}{T} \times 10^5$	Weight (mg)	Loss in weight (mg)	k (min^{-1})	$\frac{W_0 - W_{500}}{W_t - W_{500}}$
0		500.000	0		
37.439	161 220	445.000	55.000	1.469	1 143
37.805	160.429	431.250	68 750	1 819	1.185
38.171	159.650	417 500	82 500	2 161	1.231
38.536	158 879	403.750	96 250	2.498	1.280
38 902	158.120	390.000	110.000	2 828	1.333
39 268	157 359	376.250	123 750	3.151	1 391

TABLE 4

Thermal degradation data of Iraq cotton (sample 3)
Particle size = 0.063–0.125 mm; $W_0 = 500$ mg; $W_{500} = 60$ mg

Time (min)	$\frac{1}{T} \times 10^5$	Weight (mg)	Loss in weight (mg)	k (min^{-1})	$\frac{W_0 - W_{500}}{W_t - W_{500}}$
0		500.000	0		
36 232	163.940	458.029	41.971	1.158	1.105
56 715	162 514	446.708	53.292	1 452	1.138
37.198	161 609	433 069	66.931	1.799	1.179
37 681	160.650	417.290	82 710	2 195	1 232
38.164	159.849	393.377	106 623	2.794	1.268
38 647	159.199	388.823	111.177	2 877	1.304

TABLE 5

Thermal degradation data of Iraqi cotton (sample 4)
Particle size = 0.125–0.250 mm, $W_0 = 530$ mg; $W_{500} = 60$ mg.

Time (min)	$\frac{1}{T} \times 10^5$	Weight (mg)	Loss in weight (mg)	k (min^{-1})	$\frac{W_0 - W_{500}}{W_t - W_{500}}$
0		530.000	0		
36 585	163.130	491.238	38.762	1 060	1 090
37.073	161 620	474.531	55.469	1.496	1.134
37 561	160.549	462.728	67 272	1 791	1 189
37 805	159.619	445.171	84.829	2.244	1 220
38.048	158 449	422 146	107.854	2.835	1 255
38 292	157.359	393.664	136.336	3 560	1.298

TABLE 6

Thermal degradation data of Iraq cotton (sample 5)

Particle size = 0.250–0 500 mm; $W_0 = 540$ mg; $W_{500} = 90$ mg.

Time (min)	$\frac{1}{T}\times10^5$	Weight (mg)	Loss in weight (mg)	k (min^{-1})	$\frac{W_0 - W_{500}}{W_t - W_{500}}$
0		540.000	0		
36 585	163.650	497 792	42.208	1.154	1.104
36 829	162 559	487.714	52 286	1 420	1 131
37.012	161 750	464.785	65.215	1 762	1 169
37 134	161.229	462.041	77.959	2 099	1 210
37.280	160.619	449.118	90.882	2 438	1 253
37.402	160 119	436 558	103.442	2.766	1 298

TABLE 7

Thermal degradation data of Iraq cotton (sample 6)

Particle size = 0.500 mm, $W_0 = 665$ mg; $W_{500} = 70$ mg.

Time (min)	$\frac{1}{T}\times10^5$	Weight (mg)	Loss in weight (mg)	k (min^{-1})	$\frac{W_0 - W_{500}}{W_t - W_{500}}$
0		665 000	0		
33.810	168.418	625.334	39 666	1 173	1.197
34 048	167 839	615.417	49 583	1.456	1.220
34 286	167 265	605 500	59.500	1.735	1 248
34.524	166 694	595.583	69 417	2 011	1.265
34.762	166.127	585 666	79.334	2.282	1 290
35.000	165.564	575.749	89 251	2 550	1 315

TABLE 8

Thermal degradation data of extracted cellulose (sample 7)

$W_0 = 320$ mg, $W_{500} = 20$ mg

Time (min)	$\frac{1}{T}\times10^5$	Weight (mg)	Loss in weight (mg)	k (min^{-1})	$\frac{W_0 - W_{500}}{W_t - W_{500}}$
0		320 000			
30 476	179.518	284.000	36 000	1.181	1 134
30 952	178 223	278 000	42 000	1.357	1.163
31 428	176.646	272 000	48.000	1 527	1 190
31.904	175 688	266 000	54.000	1 693	1.220
32.380	174 447	260 000	60.000	1 853	1 250
32 856	173 224	254.000	66 000	2.009	1.282

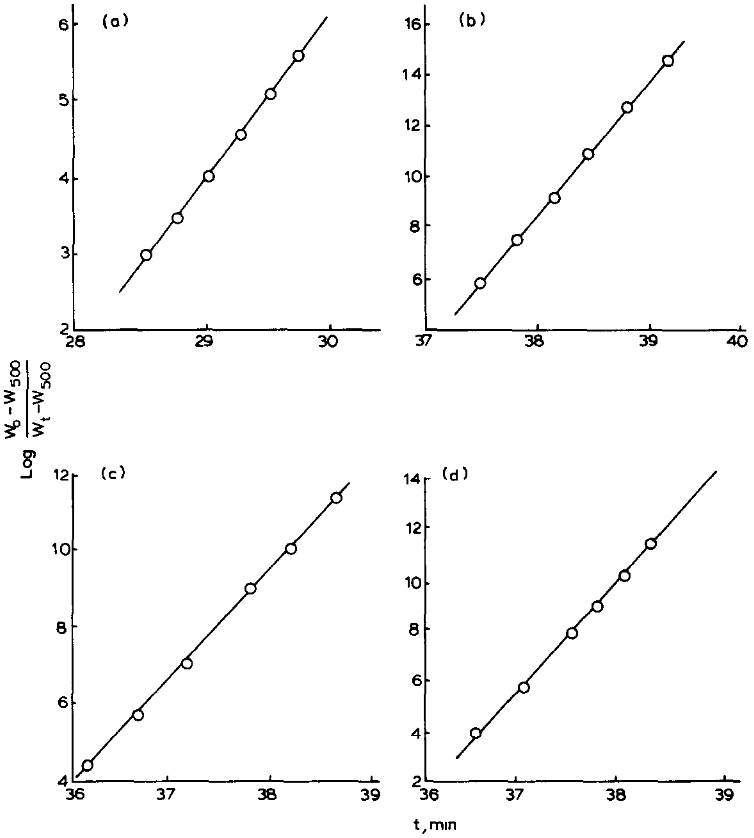

Fig. 2 The variation of $\log(W_0 - W_{500})/(W_t - W_{500})$ with time for (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4.

reaction can be expressed as

$$k = \frac{KT}{h} e^{-\Delta G^0/RT} \tag{1}$$

TABLE 9

The values of the activation energy, E_a, the change in entropy, ΔS, the change in enthalpy, ΔH, and change in free energy, ΔG, for samples 1–7

Sample no.	E_a	ΔH	ΔS	ΔG
1	32 023	30.987	126.675	−35 626
2	36.628	35.396	124.605	−41 893
3	40.041	38 629	131.636	−41 466
4	43 582	42 364	137 278	−41 786
5	50.689	49.475	148.956	−41.546
6	56.321	55.141	160 767	−40 316
7	17 847	16 740	97 810	−37 745

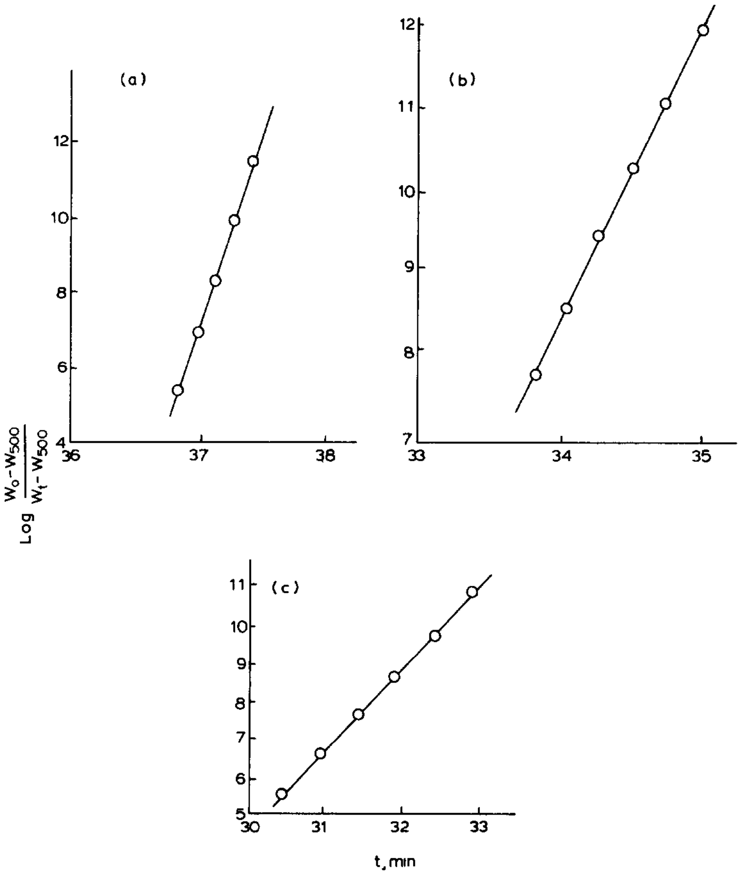

Fig 3 The variation of $\log(W_0 - W_{500})/(W_t - W_{500})$ with time for (a) sample 5; (b) sample 6, (c) sample 7

where k is the rate of reaction, K the Boltzmann constant, T the temperature, h the Planck constant, and ΔG^0 the increase in Gibbs free energy in the transfer from the initial state to the final state. If the change in free energy is expressed in terms of entropy and heat of activation, i.e. as $\Delta H^0 - T\Delta S^0$, the results is

$$k = \frac{KT}{h} e^{\Delta S/R} \cdot e^{-\Delta H^0/RT} \tag{2}$$

For a first-order reaction, the activation energy is related to the change in the heat of activation [17] by the equation

$$E_a = \Delta H^0 + RT \tag{3}$$

The rate of reaction may therefore be written as

$$k = \frac{KT}{h} e^{\Delta S/R} \cdot e^{-(E_a - RT)/RT} \tag{4}$$

or

$$k = e \cdot \frac{KT}{h} e^{\Delta S/R} \cdot e^{-E_a/RT} \tag{5}$$

From eqns (1)–(5), the thermodynamic functions, ΔS^0, ΔH^0 and ΔG^0 can be calculated.

Table 9 gives the values of the activation energy, E_a, the enthalpy change, ΔH, the entropy change, ΔS, and the free energy change, ΔG, for all samples. From these data, it is observed that as the degree of crystallinity increases, the activation energy decreases. The difference between the highest and lowest values of the activation energy for Iraq cotton samples (samples 2–6) is 19.693 kcal mole^{-1}. This difference may be considered to be used in breaking the crystalline parts of cellulose to a finer structure. Meanwhile, when representing the variation of ΔS with the crystallinity, Fig. 4 results. It is clear that the parameter of ordering and disordering structure, ΔS, increases as the degree of crystallinity increases.

The activation energies for the powdered cellulose (sample 1) and fine Iraq cotton (sample 2) are equal to 32.02 and 36.62 kcal mole^{-1}, respectively. This difference may be due to the higher purity, or the higher percentage of α-cellulose for sample 1 than for sample 2. The considerably lower value of 17.84 kcal mole^{-1} for the activation energy of the extracted cellulose (sample 7) may be attributed to

(1) the presence of some lignin compounds which softens cellulose chains;

(2) the presence of some volatile materials; and/or

(3) the lower value of the degree of polymerisation or the degree of crystallinity than the other samples.

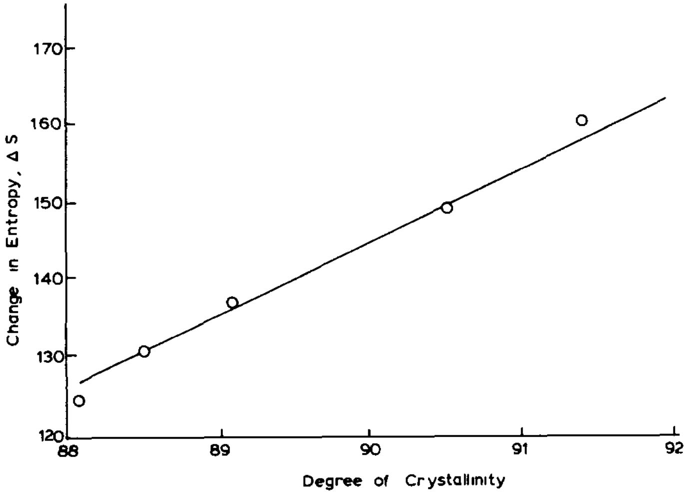

Fig. 4 The variation of ΔS with the degree of crystallinity for Iraq cotton samples.

Finally, the negative sign of ΔG indicates that the free energy of the ash, the final state, is lower than that of the initial sample.

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