STUDY OF THE THERMAL DECOMPOSITION OF CELLULOSE-HYPHAN AND ITS COMPLEXES WITH SOME TRANSITION AND INDIUM METAL IONS

I. M. M. Kenawy, M. A. H. Hafez and Kh. S. El-Said

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Abstract

The studied complexes formed by the chelating ion exchanger were characterized by reflectance and infrared spectrometry. The thermal degradation of pure cellulose–hyphan (CH) and its complexes with Hg^{2+}, In^{3+}, Cr^{3+}, Mo^{4+} and Mn^{2+} under an atmosphere of air has been studied using thermal gravimetry (TG) and differential thermal analysis (DTG). The results showed that four different stages are accompanying the decomposition of (CH) and its complexes with the studied metals. These stages were found to be affected by the presence of the investigated metal ions. On the bases of the applicability of a non-isothermal kinetic equation it was found to be a first-order reaction with the rate of degradation, k, ranging from $8.3 \cdot 10^{-5}$ to $6.2 \cdot 10^{-3}$ for (CH) and from $1.7 \cdot 10^{-5}$ to $6.6 \cdot 10^{-3}$ s^{-1} for its complexes. The activation energy, E_a, the entropy change, ΔS°, the enthalpy change, ΔH° and Gibbs free energy, ΔG° are calculated by applying the rate theory of the first-order reaction. The effect of the different central metal ions on the calculated thermodynamic parameters is discussed.

Keywords: cellulose–hyphan polymer, indium and transition metal complexes, thermal analysis

Introduction

Thermogravimetric analysis (TG) is widely used as a method to investigate the thermal analysis of polymers and cellulose and to determine some kinetic and thermodynamic parameters [1–6]. The study of organometallic compounds in the solid state by qualitative and quantitative thermochemical analysis has recorded considerable attention by the chemists [7, 8]. The majority of compounds including complexes suffer physical and chemical changes when subjected to heat energy. In spite of the fact that some authors studied TG and DTG of some organometallic compounds [9, 10], yet a little work was found in the literature concerning thermal analysis on related metal complexes [13, 14]. The importance of thermal analysis study of organometallic compounds comes from the fact that it gives a relationship between the chemical composition,

structure and material processing with those properties suitable for different technological and industrial applications. However, cellulose hyphan was used as an analytical reagent for preconcentration of trace transition, noble, and rare earth metal ions from aqueous solution [15–17]..

The aim of the present work was the preparation, isolation and thermal study of cellulose hyphan and its complexes of Hg^{2+}, In^{3+}, Cr^{3+}, Mo^{4+} and Mn^{2+}. The kinetic and thermodynamic parameters of the prepared complexes were calculated. In addition, the effect of the different central metal ions on both complexes stability and the calculated thermodynamic parameters during thermolysis are discussed.

Experimental

Cellulose hyphan (CH, (I)) ion exchanger, 1-(2-hydroxyphenylazo)-2-naphthol was obtained from (TM of the Riedel-de Haen AG, Hannover, Germany). Complexes of (CH) with $HgCl_2$, $InCl_3$, $Cr_2(SO_4)_3$ and $MnSO_4$ were prepared in the same way as described previously [16]. $[Mo(H_2O)_6]^{4+}$ solution was prepared by dissolving K_2MoCl_6 salt in aqueous CF_3SO_3H which was then separated as the yellow Mo^{4+} aq. ion from Cl^- ions on a cation-exchange column.

(I.)
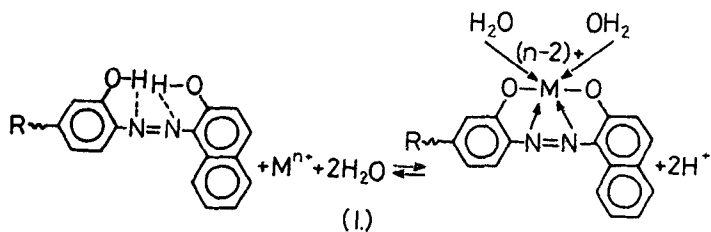
Metal complex,(A)

$\underline{M}^{n+}$= Hg(II.) , In(III.) , Cr(III.) , Mo(IV.) and Mn(II.)
$\underline{R}$ =$(C_6H_{10}O_5)_n$, cellulose.
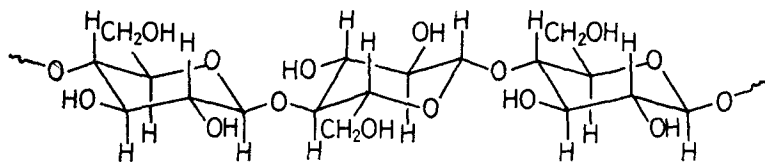
(II.)
Cellulose

IR absorption spectra were measured using a Pye Unicam spectrophotometer model 2000 using a dried nujol. Standard nujol alone was analysed for comparison with the studied samples. Thermal decomposition of (CH) and its complexes was investigated by TG and DTG thermoanalyser DT40 Schimadzu,

Japan in presence of atmospheric air. Samples were placed in a standard platinum crucible of the instrument fitted with Pt–Pt Rh (10%) thermocouple. The weight of the taken samples varied from 3.0–6.5 mg. The rate of heating was adjusted at 10 deg·min^{-1}. All other experimental conditions were as described previously [12, 16, 17].

Results and discussion

IR absorption spectra measurements have been used to characterize the complexes formed between (CH) and Hg^{2+}, In^{3+}, Cr^{3+}, Mo^{4+} and Mn^{2+} ions. The spectrum of (CH) exhibits a medium band at 1425 cm^{-1} due to the ν (N=N) vibration [18]. This band exhibits a blue shift by 10–15 cm^{-1} in the spectra of complexes. Also, the (CH) shows a broad band at 3400 cm^{-1}, which may be attributed to the different vibration modes of OH group [18]. Such broadness may be due to the presence of intramolecular hydrogen bonding between the azo
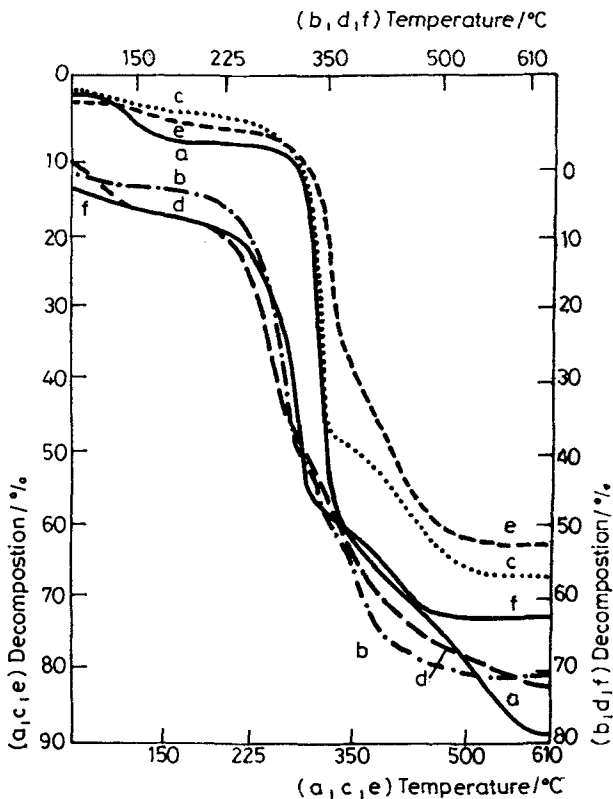

Fig. 1 TG curves of cellulose hyphan and its complexes CH (a), CH–Hg (b), CH–In (c), CH–Mn (d), CH–Mo (e) and CH–Cr (f)

group and the ortho hydroxyl groups of the cellulose–hyphan (I). The decrease in the stretching vibration of the –OH by 20–30 cm^{-1} and also the formation of less broad band at 3380–3370 cm^{-1} in the spectra of the investigated complexes confirms the absence of hydrogen bonding with participation of both –OH groups in the coordination process. This indicates that both the N=N and the –OH groups take part in the complexation with all the studied transition and indium metal ions (A).
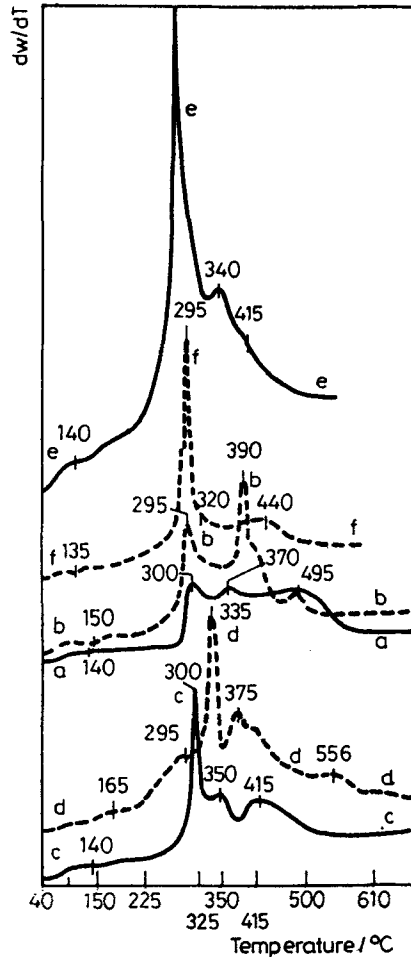

Fig. 2 DTG curves of cellulose hyphan and its metal complexes CH (a), CH–Hg (b),
CH–In (c), CH–Mn (d), CH–Mo (e) and CH–Cr (f)

The complexation process between (CH) and all the studied metal ions were also confirmed by the reflectance spectra. The reflectance spectrum of (CH)

shows a band maximum at 520 nm; whereas the a spectra of all its complexes with the investigated metal ions exhibit band maxima at 500 and 540 nm, respectively.

The thermal decomposition of (CH) and its complexes is represented in Figs 1 and 2 respectively. It appears that during heating of (CH), the TG and DTG curves undergo a series of thermal changes associated with a weight loss. These curves show that the (CH) has a series of decomposition steps starting at 140°C and finishing at ~600°C. The first broad endothermic peak located at 140°C accompanying with 10% weight loss corresponding to the evolution of adsorbed water molecules. As the temperature increases, the DTA curve shows three endothermic peaks at 300, 370 and 495°C. These three peaks are accompanied with ~78% weight loss after the first step corresponding to the degradation of (CH) along the rupture of the bonds. These three parts may correspond to the three steps which are suggested by Chatterjee [19] to represent the thermal degradation of cellulose as follows:

First step

$$A \rightarrow B_1 \text{ initiation (volatile product)}$$
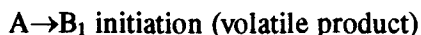
Second step: propagation (thermal degradation):

$$B_1 \rightarrow B_2 + L$$

$$B_2 \rightarrow B_3 + L$$

$$B_n \rightarrow B_{n+1} + L$$

$$\sum B_n \rightarrow \sum B_{n+1} + L$$

Third step

$$\sum B_{n+1} \rightarrow \text{carbonisation (ash)}$$

where A denotes the initial molecules of cellulose, $B_1 \ldots B_n$ are fragmented molecules and L denotes volatile products.

The broad endothermic peak above 495°C accompanied by 11% weight loss may be due to the decomposition of stable intermediate fragment (ash), Table 1.

Thermal decomposition of the complexes of (CH) with some transition metal and indium ions has been carried out following the same described experimental conditions used for (CH) alone. The experimental results are shown in

Figs 1 and 2 compared with (CH). The maximum temperature for different degradation stages are shown in Table 1. From Table 1 and the set of curves, some trends and conclusions may be suggested.

Table 1 Maximum temperature, residue percentage and final product of different decomposition stages of cellulose–hyphan (CH) and its metal complexes

Complex	Maximum temperature / °C				Residue / %	Final product
	1st stage	2nd stage	3rd stage	4st stage		
CH	140	300	370	495	11.0	–
CH–Hg	150	295	390	495	28.5	HgO
CH–In	140	300	350	415	33.4	In_2O_3
CH–Mo	140	280	340	418	37.1	Mo_2O_3
CH–Mn	165	295	335	375	27.0	MnO_2
CH–Cr	135	295	320	440	37.5	Cr_2O_3

i) The maximum temperature of the first stage is nearly the same for (CH) and all of its complexes, except for CH–Mn complex. This may be due to the stabilization of complex caused by the half-filled $(3d^5)$ orbital of Mn^{2+} ion. Hence the first decomposition stage of complexes may be interpreted by the removal of water molecules.

ii) The maximum temperature of the second stage indicates approximately the same value in case of complexes, while it has a lower value than that of free (CH). This means that at this stage the same intermediate fragments are formed.

iii) The maximum temperature of the third stage for these complexes is observed at lower value compared to the free (CH) except for CH–Hg complex which has a higher temperature value (Table 1). This result may be attributed to the catalytic effect of all the investigated metal ions during this decomposition stage with the exception of mercury ion which makes stabilization of intermediate fragments during such a stage. This may be attributed to the stabilization of complex fragments of mercury caused by its complete-filled $(5d^{10})$ orbital.

iv) The trend of the fourth stage and the explanation of such a decomposition step is similar to that of the third one (Table 1). The higher values of residue from CH–Cr and CH–Mo complexes may enhance the decomposition process of the third intermediate fragment to complete thermolysis. On the other hand, the small residue from the decomposed CH–Mn enhances the forth step to a lower temperature value compared to the free (CH) ligand.

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 the polymer can be represented by the equation:

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

Thus, the general rate expression may be written [20]

$$R_t = -\frac{dW}{dt} = \frac{A}{R_H} e^{-E_a/RT} \cdot W^n \tag{1}$$

where W is weight of active material remaining for a particular reaction, R_H is the rate of heating, R_t is the rate of decomposition, S^{-1}. (dW/dt) is the rate of degradation, T is the absolute temperature, K. A is the frequency factor, E_a is activation energy, R is the gas constant, and n is the reaction order.

The above equation can be arranged to give:

$$\ln R_t = \ln A - E_a/RT + n \ln W \tag{2}$$

when W is kept constant, and application of non-isothermal kinetic equation [20],

$$\ln \alpha - 2\ln T = \ln A - E_a/RT \tag{3}$$

where α is the weight loss percentage.

Table 2 Values of activation energies E_a of various decomposition steps of CH and its metal-complexes

Complex	E_{a1}	E_{a2}	E_{a3}	E_{a4}	E_{total} / kJ·mol^{-1}
CH	23.94	89.18	4.46	10.87	128.95
CH–Hg	24.17	52.04	4.92	13.91	95.04
CH–In	3.98	61.64	4.15	9.92	79.69
CH–Mo	8.08	44.55	4.94	11.78	69.35
CH–Mn	11.00	20.94	9.94	15.37	62.25
CH–Cr	2.95	49.66	4.48	12.14	69.23

Equation (3) requires the plotting of $(\ln \alpha - 2\ln T)$ vs. $1/T$ for the second step to be linear as is experimentally observed (Fig. 3). A good linear regression with linear correlation coeffficient (r) between 0.98 to 0.99, associated with breaks of straight lines were obtained. The calculated values of activation ener-

gies of each stage together with the total activation energies of the whole stages of (CH) alone and CH–metal complexes are shown in Table 2.

The magnitude of the activation energy measured for solid phase decomposition reaction has often been explained by the energy barrier in the limiting step, e.g. bond rupture, electron or proton transfer or enthalpy of decomposition. The E_a values obtained were found to be in good agreement with that of the thermolysis processes. The higher activation energy in case of CH–Hg and CH–In complexes indicates the high stability of such chelates as well as the lower catalytic effect of such metals for the thermal decomposition of their corresponding chelates. From Table 3, one observes that the total activation energy of decomposition of (CH) ligand is higher than that of CH–metal complexes. This indicates that all the investigated metal ions act as catalysts to accelerate the decomposition process of such chelates.

Table 3 Summary of total activation energy, ionic radius, effective nuclear charge (Z) and effective field strength (F) of the studied metal ions

Ion	E_{total} / kJ·mol^{-1}	r /Å	$F = Z/r^2$
Hg^{2+}	95.04	1.12	3.60
In^{3+}	79.69	0.81	7.62
Mo^{4+}	69.35	0.68	7.46
Mn^{2+}	62.25	0.80	5.63
Cr^{3+}	69.23	0.69	7.25

The total activation energies of the decomposed chelates as calculated by Chatterjee's method [19] can be arranged according to the following sequence:

$$CH–Cr(III) < CH–Mn(II) < CH–Mo(IV) < CH–In(III) < CH–Hg(II)$$

This arrangement with the exception of Cr(III) is in good agreement with the Irving-Williams series [22]. This difference in activation energies may be due mainly to two factors:

i) The variation in effective electric field strength, $F = Z/r^2$ where Z and r are the effective nuclear charge and radius of cation respectively [23] which is shown in Table 3. One may expect that with the increase in F (Table 3) the stability of complexes increases which is in good agreement with our results with the exception of Hg^{2+} (Table 3). This arrangement is in good agreement with the sequence of thermal stabilities given in this work.

ii) The covalent character of the bonds between the metal ion and the heteroatoms of the (CH) ligand i.e. N=N and –OH. In the case of Hg^{2+} the cova-

lent bonds formed between the metal ion and the heteroatoms of the CH ligand are much stronger than the other studied metal ions. The latter factor explains the higher stability and increasing activation energy of such metal ion than the other investigated metal ions (Table 3) [14].
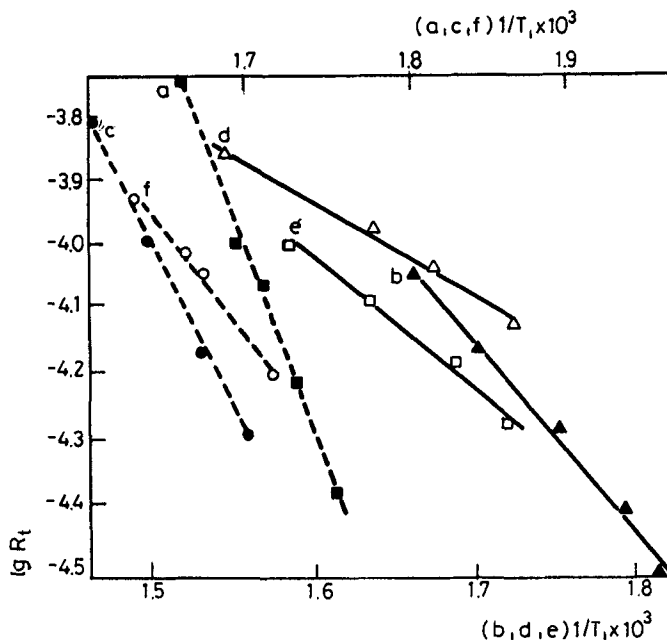

Fig. 3 The variation of log R_t with $1/T$ of the 2nd step for cellulose hyphan and its metal complexes CH (a), CH–Hg (b), CH–In (c), CH–Mn (d), CH–Mo (e) and CH–Cr(f)

Table 4 Values of specific rate constant, k, s^{-1} and $t_{1/2}$, s of various decomposition steps of CH and its metal-complexes

Complex	1st stage		2nd stage		3rd stage		4st stage	
	$k \cdot 10^3$	$t_{1/2}$	$k \cdot 10^3$	$t_{1/2}$	$k \cdot 10^3$	$t_{1/2}$	$k \cdot 10^5$	$t_{1/2}$
CH	3.2	2.38	6.2	1.90	0.27	42.50	8.9	129.3
CH–Hg	4.5	2.57	3.8	3.04	0.70	16.13	2.1	464.0
CH–In	1.5	8.11	6.7	1.73	0.30	39.40	11.5	101.8
CH–Mo	2.0	5.72	2.8	3.97	0.25	47.20	2.4	481.7
CH–Mn	3.3	3.45	1.7	6.93	0.12	94.00	5.7	203.3
CH–Cr	0.5	26.76	3.3	3.45	0.35	33.86	4.3	237.2

Table 5 Values of the entropy change ΔS°, enthalpy change ΔH° and free energy change ΔG° of various decomposition steps of CH and its metal-complexes

Complex	1st step ΔS_1°	2nd step ΔS_2°	3rd step ΔS_3°	4st step ΔS_4°	ΔS_{total}° / $J\cdot mol^{-1}\cdot K^{-1}$
CH	57.97	155.64	7.71	14.15	235.47
CH–Hg	57.17	91.62	7.42	18.11	174.29
CH–In	9.64	107.57	6.66	14.42	138.29
CH–Mo	19.56	80.56	8.06	17.05	125.23
CH–Mn	36.53	36.87	16.35	23.72	113.14
CH–Cr	7.23	87.43	7.56	17.03	119.25

Complex	1st step ΔH_1°	2nd step ΔH_2°	3rd step ΔH_3°	4st step ΔH_4°	ΔH_{total}° / $kJ\cdot mol^{-1}$
CH	20.51	84.42	– 0.39	4.49	109.03
CH–Hg	20.65	47.32	– 0.59	7.53	74.91
CH–In	0.55	56.87	–1.03	4.20	60.55
CH–Mo	4.65	39.95	– 0.16	6.04	50.47
CH–Mn	12.36	16.22	4.85	9.98	43.45
CH–Cr	– 0.44	44.87	– 0.45	6.21	50.26

Complex	1st step ΔG_1°	2nd step ΔG_2°	3rd step ΔG_3°	4st step ΔG_4°	ΔG_{total}° / $kJ\cdot mol^{-1}$
CH	–3.43	– 4.76	–5.35	–6.38	–19.92
CH–Hg	–3.52	– 4.72	–5.51	–6.38	–20.92
CH–In	–3.43	– 4.77	–5.18	–5.72	–19.05
CH–Mo	–3.43	– 4.60	–5.10	–5.74	–18.87
CH–Mn	– 4.08	– 4.72	–5.09	–5.39	–19.28
CH–Cr	–3.39	– 4.79	– 4.93	–5.93	–19.04-

The thermodynamic parameters were calculated from the rate theory [24] and are summarized in Table 5.

Again a plot of log R_t vs. time (s) gives straight lines for all four steps of decomposition of (CH) and its metal complexes. Figure 4 shows the variation of log R_t with time of the second step as an example of the four decomposed steps for (CH) and its chelates with the studied metal ions. This linearly confirms the suggested first-order rate constants of the thermal decomposition process. The

value of the specific rate of reaction, k and consequently $t_{1/2}$ can be calculated from the slope of the figures obtained (Table 4).
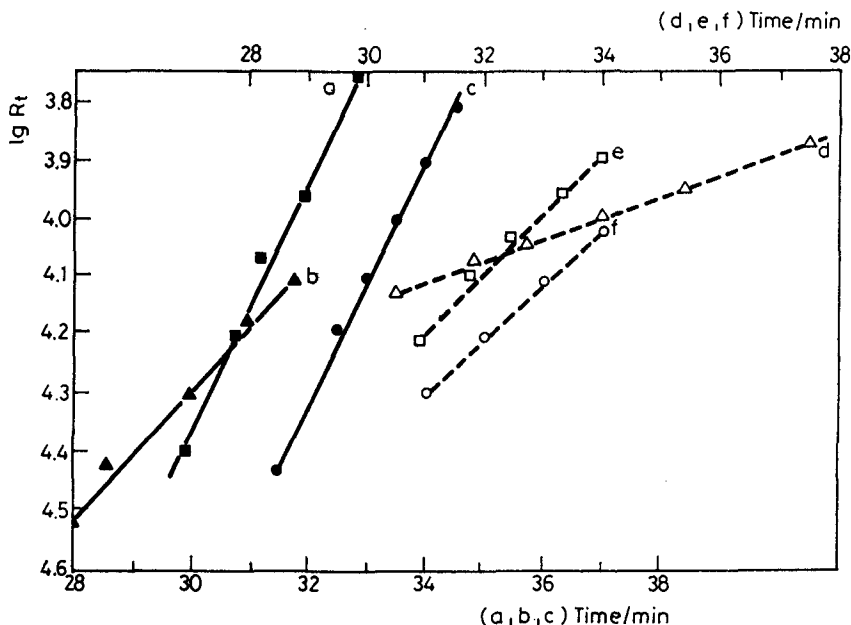

Fig. 4 The variation of log R_t with time of the second step for cellulose hyphan and its complexes CH (a), CH–Hg (b), CH–In (c), CH–Mn (d), CH–Mo (e) and CH–Cr (f)

The positive values of entropy change, $\Delta S°$, observed in Table 5 may suggest that the disorder of the decomposed fragments increases much more rapidly than that of the undecomposed ones. Again, the smaller $\Delta S°$ values of the CH–complexes compared with that of the free ligand suggest that these metal ions play a role in the disordering of the decomposed fragments. The positive sign of $\Delta H°_{total}$ of the whole four decomposition steps for (CH) and its complexes as shown in Table 5, indicates that the decomposition stages are endothermic processes.

The negative sign of $\Delta G°$ indicates that the free energy of the final residue is lower than that of the initial compound, and, hence all the decomposition steps may be spontaneous processes.

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Zusammenfassung — Die durch einen chelatbildenden Ionenaustauscher gebildeten untersuchten Komplexe wurden mittels Reflexionsmessung und IR-Spektroskopie charakterisiert. Mittels TG und DTG wurde in Luft der thermische Abbau reinem Zellulose-Hyphan (CH) und seiner Komplexe mit Hg^{2+}, In^{3+}, Cr^{3+}, Mo^{4+} und Mn^{2+} untersucht. Die Ergebnisse zeigen, daß die Zersetzung von (CH) und seiner Komplexe mit den untersuchten Metallen von vier verschiedenen Stufen begleitet wird. Diese Stufen werden von der Gegenwart der untersuchten Metallionen beeinflußt. Ausgehend von der Anwendbarkeit einer nichtisothermen kinetischen Gleichung wurde eine Zersetzungsreaktion erster Ordnung mit einer Geschwindigkeitskonstante zwischen $8{,}310^{-5}$ und $6{,}210^{-3}$ für (CH) und zwischen $1{,}710^{-5}$ und $6{,}610^{-3}$ für seine Komplexe gefunden. Die Aktivierungsenergie E_a, die Entropieänderung ΔS°, die Enthalpieänderung ΔH°, die freie Energie ΔG° wurden durch Anwendung der Geschwindigkeitstheorie auf die Reaktion erster Ordnung berechnet. Der Einfluß der verschiedenen zentralen Metallionen auf die berechneten thermodynamischen Größen wurde diskutiert.