Journal of Thermal Analysis, Vol. 36 (1990)1257-1264

THERMAL DECOMPOSITION OF CELLULOSE HYPHAN AND ITS COMPLEXES WITH RARE EARTH ELEMENTS AND SCANDIUM

*A. A. Said** and *I. M. Kenawy***

CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE UNITED ARAB EMIRATES
UNIVERSITY, AL-AIN P. O. BOX 15551, U.A.E.

(Received November 24, 1989)

Thermal decomposition of cellulose hyphan (CH) and its complexes with Lu, Gd, Nd and Sc under an atmosphere of air has been studied using thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA). The results showed that, a different stages are accompanying the decomposition of (CH) and its complexes. These stages are affected by the presence of the metal ions. On the basis of the applicability of a non-isothermal kinetic equation, it was demonstrated that three main stages are involved in the decomposition processes. The activation energies of the different stages are calculated.

The study of organometallic compounds in the solid state by qualitative and quantitative thermochemical methods has received considerable attention. The majority of compounds, including complexes, suffer physical and chemical changes when subjected to heat energy. A little work was found in the literature concerning thermal analysis, even on related metal complexes. Amazingly, although thermogravimetry (TG) and differential thermal analysis (DTA) are versatile techniques, their application to the study of organometallic compounds has been scarcely attempted [1-3]. The interest of the thermal analysis study of organometallic compounds aims to relate composition, structure and material processing with those properties suitable for various technological application.

Permanent address: *Chemistry Department, Faculty of Science, Assiut University, Assiut Egypt.

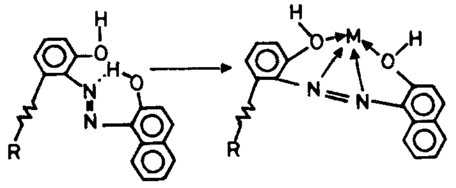
** Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

However, cellulose hyphan was used as analytical method for the preconcentration of transition metal ions [4] as well as noble metal [5]. Recently the isolation of rare earth elements and scandium from aqueous solution by cellulose hyphan ion exchanger has been achieved [6]. The results showed that, its selectivity to the complex formation takes the following order Lu > Gd > Sc > Nd. In fact, little data have been published on the thermal decomposition of cellulose hyphan and its complexes with metal ions. Therefore, the present work was devoted to describe the thermal decomposition of cellulose hyphan and its complexes with Lu, Gd, Nd and Sc. On addition, possibly to understand the effects of these metal ions on the complexes stability during their thermolysis.

Experimental

Cellulose hyphan (CH) ion exchanger, 1-(2-hydroxypherylazo)-2-naphthol, was obtained from (IM of the Riedel-de Haen AG, Hannover, West Germany). Complexes of (CH) with Lu, Gd, Nd and Sc were prepared as previous method [6].



Cellulose Hyphan Metal complex

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 with REE's and Sc was investigated by differential thermal analysis (DTA), thermoanalyser GDTA 16 (Setaram, Lyon, France) in presence of air atmosphere. Sepecimens were placed in a standard platinum crucible of the instrument fitted with Pt-PtRh (10%) thermocouple. The weight of the samples taken varied from 3-5 mg and the rate of heating was 7 deg.min^{-1}. All the runs were made with Al_2O_3 calcinated at 1300° as a reference.

Results and discussion

IR absorption spectra measurements have been used to characterize the complexes formed between (CH) and Lu, Gd, Nd and Sc metal ions. Figure 1 shows the spectrum of the (CH) and the spectra of extracted solid complexes after complete dryness. Curve (a) corresponds to (CH), the band assigned at 1210 cm^{-1} attributed to the stretching vibration of azo group (–N=N–) and the band assigned at 3375 - 4000 cm^{-1} corresponds to the stretching vibration of hydrogen bond of hydroxyl group [7]. Curves (b, c, d and e) are correspond to the complexes of (CH) with Lu, Gd, Nd and Sc respectively. These curves indicate that the band assigned at 1210 cm^{-1} of (–N=N–) is shifted to 1200-1205 $cm^{-1.}$ This shift indicates the participation of this group in coordination. On addition the shift in the ν_{OH} band is appreciably high 25-30 cm^{-1} to the lower for all metal chelates, also, the band becomes less broad than that of the (CH) alone. This indicates that both the (–N=N–) and the (–OH) group take part in the coordination with all the studied metal ions.

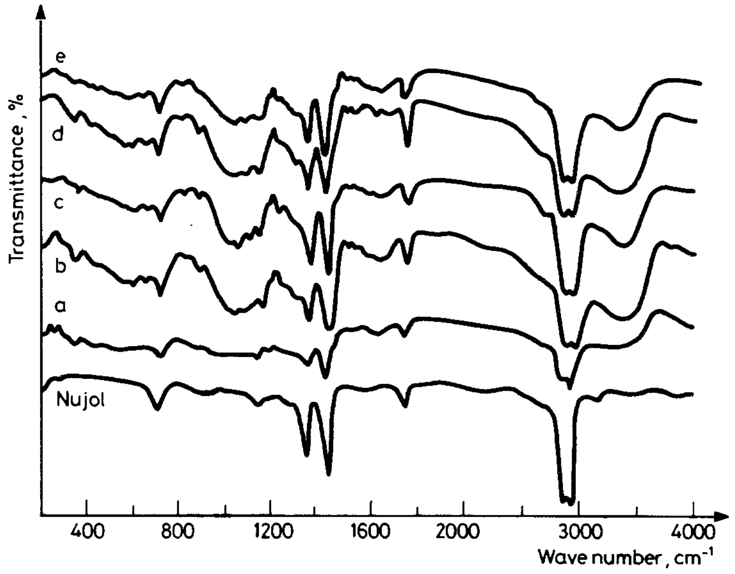


Fig. 1 The infrared absorption spectra of cellulose hyphan (a) and its complexes with Lu (b), Gd (c), Nd (d) and Sc (e)

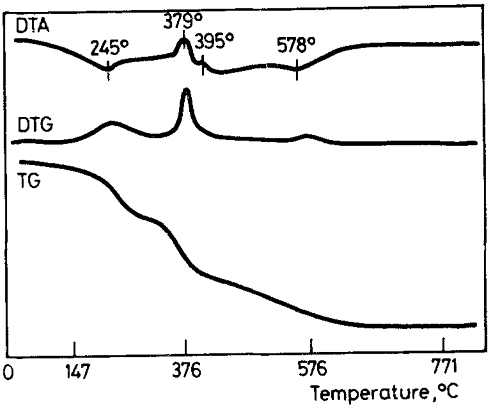


Fig. 2 TG, DTG and DTA curves of cellulose hyphan

Thermal decomposition of (CH) is represented in Fig. 2. It appears that during heating of (CH), the DTA curve undergoes a series of thermal changes associated with a weight loss in the TG and DTG curves. These curves show that, the (CH) has a series of decomposition steps starts at 130° and finished at ≃ 600°. The first broad endothermic peak located at 245° accompanying with ≃ 30% weight loss–corresponds to the evolution of water

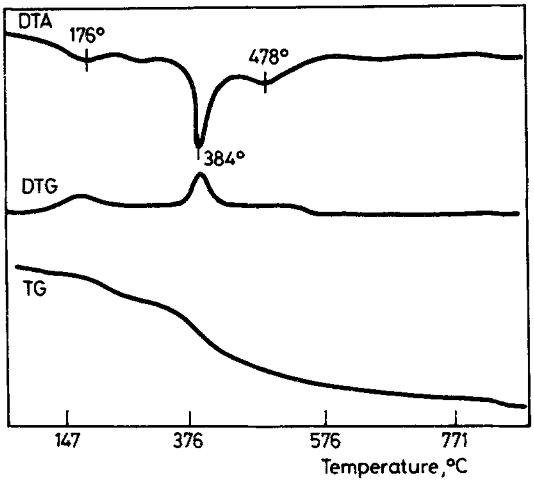


Fig. 3 TG, DTG and DTA curves of cellulose hyphan complex with Lu^{3+} ion

molecules. As the temperature is raised, the DTA curve shows two exothermic peaks at 379° and 395°. These two peaks are accompanied with ≃ 50% weight loss correspond to the degradation of (CH) along the rupture of the bonds. The broad endothermic peak at 580° is accompanied with 20% weight loss, may be due to the decomposition of the stable intermediate fragment.

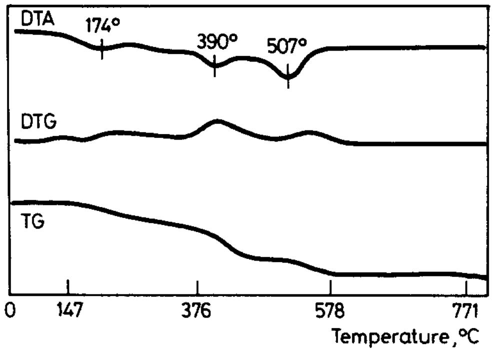


Fig. 4 TG, DTG and DTA curves of cellulose hyphan complex with Gd^{3+} ion

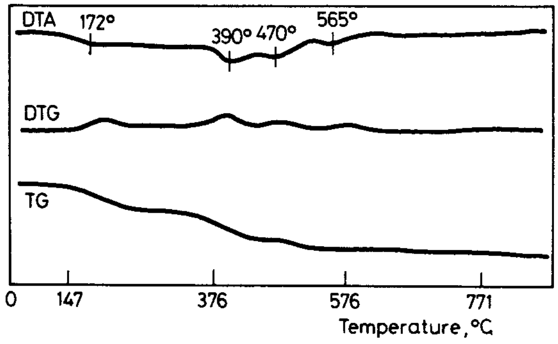


Fig. 5 TG, DTG and DTA curves of cellulose hyphan complex with Nd^{3+} ion

Thermal decomposition of the complexes of (CH) with the metal ions has been carried out using the same conditions mentioned above. The experimental results are shown in Figs (3, 4, 5 and 6) for Lu, Gd, Nd and Sc respectively. The maximum temperatures of the different decomposition stages are cited in Table 1.

Table 1 The maximum temperatures of different decomposition stages of (CH) and its complexes with REE' s and Scandium

Complex	1st stage T, °C	2nd stage T, °C	3rd stage T, °C	4th stage T, °C	Residue, %	Final product
CH-Lu	176	390	478	–	5.2	Lu_2O_3
CH-Gd	174	390	507	–	3.6	Gd_2O_3
CH-Nd	172	386	487	540	1.5	Nd_2O_3
CH-Sc	172	388	470	565	1.3	Sc_2O_3
CH-alone	245	379	445	578	0.36	-

From the above Table and looking the set of curves, some trends and conclusions may be drawn. (*i*) The maximum temperature of the first stage is nearly the same for all complexes while it has lower value than that of (CH) alone. The first decomposition stage of complexes may be attributed to the removal of water molecules of coordination. (*ii*) The maximum temperature of the second stage indicates the same value in case of complexes while it has higher value than that (CH). This means that, at this stage the same intermediate fragments are formed. (*iii*) The maximum temperature of the third stage of complexes was occurred at higher value compared to (CH) alone. This result may attributed to the stabilization of the intermediate fragments in the second step by the presence of metal ions. (*iv*) The fourth stage not observed in case of Lu and Gd while it appeared in case of Nd and Sc. This behavior can be understood if we compare the obtained amount of residue at the end of thermolysis (see Table 1). The higher values of residue from Lu and Gd may enhances the decomposition process of the third intermediate fragment to complete thermolysis. On the other hand, the small

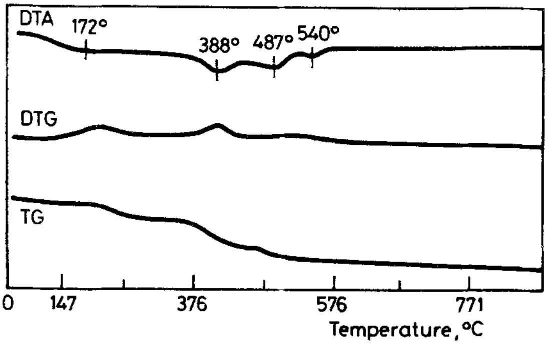


Fig. 6 TG, DTG and DTA curves of cellulose hyphan complex with Sc^{3+} ion

residue from Nd and Sc enhances the fourth step to lower temperature compared to the (CH) alone.

The application of non-isothermal kinetic equation [8],

$$\ln\alpha - 2\ln T = A_0 - E/RT$$

was checked by plotting ($\ln\alpha - 2\ln T$) as obtained from TG curves *vs* $1/T$. A good linear correlation associated with two breaking of straight lines were obtained. Such breaking indicates three decomposition processes. The calculated values of activation energies are cited, in Table 2.

Table 2 Values of activation energies of various decompositions steps of (CH) and its complexes with REE's and Sc

Complex	E_1, KJ mol^{-1}	E_2, KJ mol^{-1}	E_3, KJ mol^{-1}	E_{total}, KJ mol^{-1}	Ionic redius
CH-alone	41.60	40.96	7.02	88.58	–
CH-Lu	26.50	38.56	11.60	76.60	0.848
CH-Gd	24.10	36.30	9.77	70.17	0.938
CH-Nd	21.50	34.26	8.60	64.36	0.995
CH-Sc	27.20	32.96	9.50	69.66	0.700

The magnitude of activation energy measured for solid phase decomposition reaction has often been ascribed to the energy barrier in the limiting step, e.g. bond rupture, electron or proton transfer or enthalpy of dissociation. The comparison of *E*-values with the results of thermolysis, a good agreement is obtained. The higher activation energy in case of Lu and Gd is comparable with their final residue. Therefore, the high yield from Lu and Gd is responsible for the high stability of the chelate formed with cellulose hyphan. Furthermore, the stability of Lu and Gd complexes should need higher energies compared to the other complexes. This behaviour is in agreement with lanthanides contractions [9]. In case of Sc complex shows some difference from those lanthanides [10]. The comparison of Sc ionic radius with the ionic radii of Lu, Gd and Nd, its behaviour can be understood.

The interest result is the summation of the activation energies of the different stages of REE's and Sc complexes takes the following order, Lu > Gd > Sc > Nd.

The comparison of this result with the selectivity of the cellulose hyphan for the isolation of these elements, the same order was obtained [6].

References

1 C. E. Carraher, Jr. Am. Chem. Soc. Div. Org. Cont. Plast. Chem. Paper, 35 (1975) 380.
2 A. M. Seyam, Dirasat, (Ser), Nat. Sci. (Univ. Jordan), 7 (1980) 107.
3 H. S.O. Chan, T. S. A. Hor, C., S. M. Chaim and T. C. Chong, J. Thermal Anal., 32 (1987) 1115.
4 K. H. Lieser, H. M. Rober and P., Burba, Fresenius Z. Anal. Chem., 284 (1977) 361.
5 I. M. Kenawy, M. E. Khalifa and M. M. El-Defrawy, Analusis, 15 (1987) 314.
6 I. M. Kenawy and M. A. H. Hafez, Anal. Sci., 5 (1989).
7 L. J. Bellamy, The Infrared Spectra of Complex Molecules., 2nd ed., (1966) 354.
8 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
9 F. A. Cotton and J. Wilkinson, Advanced Inorganic Chemistry, third edition, John Wiley and Sons, New York, London, 1976, p. 923.
10 A. Westerhof and H. J. DeLiefole Meijer, J. Organomet. Chem. Chem., 116 (1976) 319.

Zusammenfassung — Mittels TG, DTG und DTA wurde die thermische Zersetzung von Cellulosehyphan (CH) und seiner Komplexe mit Lu, Gd, Nd und Sc an Luft untersucht. Es zeigte sich, daß die Zersetzung von (CH) und seiner Komplexe von verschiedenen Schritten begleitet werden. Diese Schritte werden durch die Gegenwart der Metallionen beeinflußt. Unter der Annahme der Anwendbarkeit einer nichtisothermen kinetischen Gleichung wurde gezeigt, daß im Zersetzungsprozeß drei Hauptschritte inbegriffen sind. Die Aktivierungsenergie der verschiedenen Schritte wurde berechnet.