

THERMAL STUDIES ON SOME IONIC CHELATES OF HAFNIUM(IV)

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Abstract

Ionic chelate complexes of kojic acid(I) and hafnium(IV) of the type $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{MCl}_3]^-$ (II) [HL =kojic acid; M =Zn(II), Cd(II), Hg(II), Cu(II)] have been synthesised and characterised by spectral studies (IR, UV, ^1H NMR and ^{13}C NMR). Thermogravimetric (TG) and differential thermal analytical (DTA) studies have been carried out for these complexes and from the TG curves, the order and apparent activation energy for the thermal decomposition reactions have been elucidated. The various thermal studies have been correlated with some structural aspects of the complexes concerned. From DTA curves, the heat of reaction has been calculated.

Keywords: apparent activation energy and heat of reaction, differential thermal analysis, hafnium(IV) complexes, order of thermal reaction, thermogravimetry

Introduction

Recent studies on determination of kinetic parameters from thermal data [1–5] prompted us to analyse the variation in thermal stability of some metal complexes in terms of their structural parameters. This follows from our interest to investigate the thermal behavior of metal-biomolecule complexes [6, 7].

Experimental

The following instruments were used: Elico conductivity Bridge, model CM-180 for conductance measurements; Perkin Elmer, FTIR spectrometer, Spectrum 2000 for IR spectra; Beckman DU-64 spectrophotometer for UV spectra; Bruker spectropin advance 300 spectrometer for ^1H NMR and ^{13}C NMR spectra. Rigaku model 8150 Thermoanalyser (Thermafex) was used for simultaneous recording of TG–DTA curves in air at a heating rate of 10°min^{-1} . For TG, the instrument was calibrated using calcium oxalate while for DTA calibration was done using indium metal, both of which were

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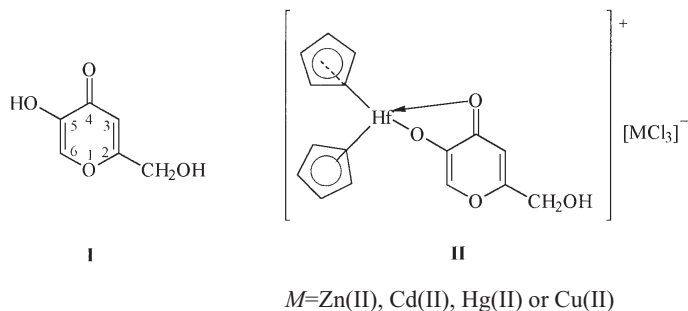
supplied along with the instrument. A flat bed type Al-crucible was used with α -alumina (99% pure) as the reference material for DTA. Kojic acid was procured from Aldrich Sigma, USA and hafnocene dichloride, $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}_2$ was purchased from Alfa products, Ventron, USA. They were used without further purification.

Preparation and characterisation of complexes

The complexes were prepared by adding slowly, the metal salt solution [ZnCl_2 (0.034 g, $0.25 \cdot 10^{-3}$ mol); CdCl_2 (0.046 g, $0.25 \cdot 10^{-3}$ mol); HgCl_2 (0.068 g, $0.25 \cdot 10^{-3}$ mol) or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.043 g, $0.25 \cdot 10^{-3}$ mol)] in acetone (10 ml) to a stirred solution of bis(η^5 -cyclopentadienyl)hafnium(IV) dichloride (0.095 g, $0.25 \cdot 10^{-3}$ mol) and kojic acid (HL, 0.035 g, $0.25 \cdot 10^{-3}$ mol) in acetone (20 mL). The contents were stirred for 4 h and filtered. From the filtrate the solvent was evaporated under vacuum at room temperature so as to reduce the volume of the filtrate to about one-quarter of the original. Petroleum ether was added to the concentrated filtrate and the mixture was left to stand overnight. The products thus obtained were washed with petroleum ether. They were then recrystallized from an acetone solution by the addition of petroleum ether.

Satisfactory results of spectral studies revealed that the complexes were of good purity, this was also supported by TLC. The complexes were yellow or brown in colour. They were soluble in THF, DMSO, DMF and partially soluble in water. Conductance measurements were determined to be of the order of $\text{ca } 30 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating that these complexes were 1:1 electrolytes in nitrobenzene.

In IR spectra, the absorption at 1660 cm^{-1} in case of the ligand was assigned to $\nu(\text{C}=\text{O})$ stretching frequency [8]. On complexation, this frequency was further lowered by $\text{ca } 45 \text{ cm}^{-1}$, indicating that the ligand chelates to the hafnium(IV) ion through C(4) carbonyl. The $\nu(\text{C}=\text{C})$ stretching frequency observed at 1580 cm^{-1} for kojic acid (I) shifted to $\text{ca } 1560 \text{ cm}^{-1}$ in the complexes (II) [9]. In the free ligand, the band due to phenolic OH stretching occurred at 3200 cm^{-1} [10] and that due to $\delta(\text{OH})$ at 1300 cm^{-1} [9]. These bands were absent in the spectra of the complexes. A weak absorption band around 490 cm^{-1} was observed in the spectra of all the complexes which may be attributed to metal-oxygen stretching vibration. Another weak band was observed around 375 cm^{-1} which was due to metal-chlorine stretching. The bands at 1282 and



1230 cm^{-1} in the ligand and complexes, respectively, were due to aromatic C–O–C stretching frequency [10].

In the UV spectra of kojic acid (I), an intense band was observed at 255 nm ($\log \epsilon = 4.8$) due to $\pi-\pi^*$ absorptions of the chromophoric carbonyl group [11]. This band shifted to ca 270 nm ($\log \epsilon = \text{ca } 3.8$) in the case of its complexes (II). The shift was attributed to the involvement of C=O group in complexation.

The ^1H NMR spectra of hafnocene complexes (II) showed signals in δ 2.55 (s, 2H, CH_2 at C(2)), δ 6.83 (s, 1H, H(3)) and δ 8.10 (s, 1H, H(6)) regions. In free kojic acid, the signals due to H(3) and H(6) have been reported in δ 6.45 and δ 7.92 regions, respectively [12]. The downfield shift in the metal complexes may be attributed to the involvement of carbonyl group at C(4) and hydroxy group at C(5) in complexation. Another signal in the region δ 6.9–7.0 was observed in the spectra of all the complexes and was attributed to the protons of the cyclopentadienyl rings.

The ^{13}C NMR spectrum of kojic acid showed absorptions due to C(4) carbonyl and C(5) carbon at 174.6 and 145.8 ppm, respectively [13]. In the complexes, the former signal shifted to ca 179.5 and the latter to ca 148.7 ppm. These results indicated that complexation involved deprotonation of C(5) hydroxyl and chelation through C(4) carbonyl. The resonance signals due to C(2), C(3) and C(6), in case of metal complexes were observed at ca 168.6, ca 109.8 and ca 139.8 ppm, respectively. The CH_2OH group absorbed at ca 59.6, while the carbon of the cyclopentadienyl ring gave a resonance signal at 122.2 ppm [14].

Results



From the TG curve it was observed that the mass change began at 379 and continued upto 695 K. The observed mass loss of 48% corresponded to the formation of a mixture of HfO_2 and ZnO , for which the calculated mass loss was 53%.

In the DTA profile two exothermic peaks with T_{max} 419 and 635 K, respectively, were observed.



From the TG curve, it was observed that the complex was thermally stable upto 369 K. Beyond this temperature, the TG curve showed a mass loss upto 669 K, which corresponded to the formation of a mixture of HfO_2 and CdO . The observed mass loss of 49% was in complete agreement with the theoretically calculated mass loss of 49%.

An exothermic peak was observed in the DTA curve of the complex with T_{max} 625 K.



The TG curve indicated that the decomposition began at 346 and continued upto 610 K. The observed mass loss of 67% corresponded to the formation of HfO_2 , as HgO volatilized at such high temperatures. The calculated mass loss for the decomposition reaction was 72%.

In the DTA profile an exothermic peak was observed with T_{max} 562 K.



From the TG curve, it was observed that the mass change began at 362 and continued upto 679 K. A mass loss of 58% was observed over this temperature range which corresponded to the formation of a mixture of HfO_2 and CuO , for which the theoretically calculated mass loss was 53%.

In the DTA profile an exothermic peak was observed with T_{max} 604 K.

Discussion

Table 1 Thermal data

Compound	Thermogravimetry			Differential thermal analysis		
	Temperature range/K	<i>n</i>	$E_a/\text{kJ g}^{-1}$	Thermal effect	T_{max}/K	$\Delta H/\text{kJ g}^{-1}$
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{ZnCl}_3]^-$	379–695	1	6.73	exothermic	419	0.0515
				exothermic	635	0.6529
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CdCl}_3]^-$	369–669	1	11.50	exothermic	625	0.4314
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{HgCl}_3]^-$	346–610	1	36.66	exothermic	562	2.8675
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CuCl}_3]^-$	362–679	1	31.90	exothermic	604	1.0575

Table 2 Mass loss data

Compound	Mass loss observed (calc./%)	Nature of products
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{ZnCl}_3]^-$	48 (53)	HfO_2 and ZnO
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CdCl}_3]^-$	49 (49)	HfO_2 and CdO
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{HgCl}_3]^-$	67 (72)	HfO_2
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CuCl}_3]^-$	58 (53)	HfO_2 and CuO

The results of the TG and DTA evaluations are compiled in Table 1 and the mass loss data are summarized in Table 2. From the TG curves, the order (*n*) and activation energy (E_a) of the thermal decomposition reaction have been elucidated by the

method of Coats and Redfern [15]. From the DTA curves the heat of reaction (ΔH) and T_{\max} have been calculated.

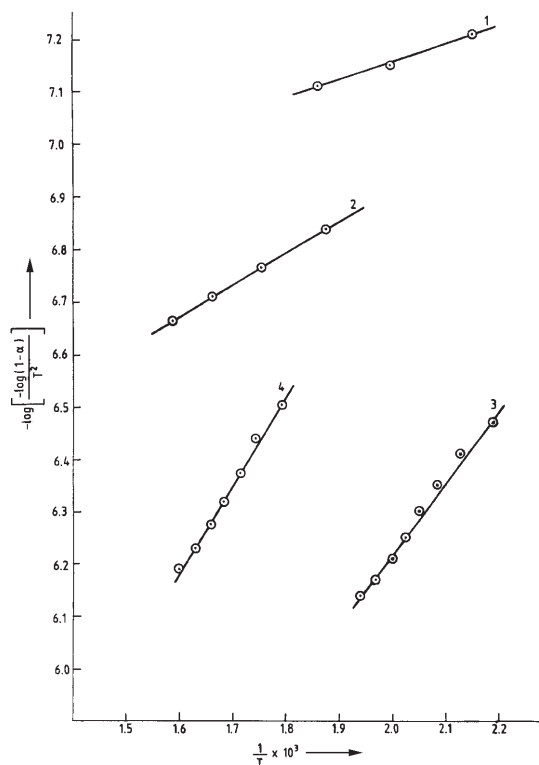
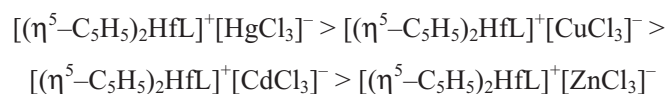


Fig. 1 Linearization curves of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{MCl}_3]^-$ complexes: 1 – $M=\text{Zn(II)}$; 2 – $M=\text{Cd(II)}$; 3 – $M=\text{Hg(II)}$; 4 – $M=\text{Cu(II)}$

The linearization curves are shown in Fig. 1. The order of reaction for the thermal decomposition of the above complexes was one. A comparison of the activation energy data for the thermal degradation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{MCl}_3]^-$ complexes revealed that the E_a values followed the order,



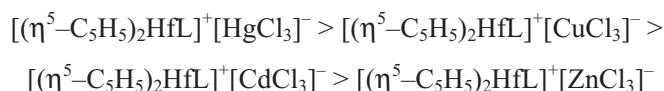
This may be explained on the basis of the fact that larger cations are stabilized by larger anions. The complex cation $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+$ is very large in size and the size of the $M(\text{II})$ ions increases in the order $\text{Zn(II)} < \text{Cd(II)} < \text{Cu(II)} < \text{Hg(II)}$. In the case of the $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{HgCl}_3]^-$ complex, the larger size of Hg(II) ion helps in effective stabilization of the complex cation and therefore gives rise to a higher lattice energy. This makes thermal degradation relatively difficult and the reaction involves a higher value of E_a . For the $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{ZnCl}_3]^-$ complex, the smaller size of the Zn(II)

ion leads to a relatively poor stabilization of the complex cation and to a comparatively lower lattice energy. Thus the thermal reaction involves a lower value of E_a .

The heat of reaction (ΔH) has been calculated for the thermal effects [16]. The temperature dependent calibration coefficient was obtained from the Curell equation [17].

Conclusions

Thermal behaviour of the complexes has been investigated and E_a values have been found to follow the order:



It was, therefore, evident that the nature of metal ion in the anionic moiety contributed to the variation in the activation energy for the thermal degradation of the complexes. The energy of activation, in turn, reflected the kinetic lability of the complexes. The compounds with lower E_a values were more labile as compared to those with higher E_a values.

The TG data of the complexes was supplemented by DTA studies. The heat of reaction (ΔH) has been enumerated from the DTA curves. The temperature dependent calibration coefficient has been obtained from the Curell equation.

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