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THERMAL STUDIES OF THE DIBUTYLTIN(IV) COMPLEXES OF SCHIFF BASES DERIVED FROM AMINO ACIDS

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Abstract

The thermal decomposition using TG, DTG and DTA, of seven complexes of the types $Bu_2SnL(I)$ and $Bu_2SnL(II)$ (where $H_2L(I)$=Schiff base derived from acetylacetone and glycine [H_2L-1(I)] or *L*-leucine [H_2L-4(I)] or methionine [H_2L-5(I)] or phenylglycine [H_2L-6(I)]; $H_2L(II)$=Schiff base derived from *o*-hydroxynaphthaldehyde and β-alanine [H_2L-2(II)] or *DL*-valine [H_2L-3(II)] or *L*-leucine [H_2L-4(II)] is shown to fall into one of two categories, viz, (1) $Bu_2SnL(I)$ complexes that decompose without melting to give SnO as the final tin containing product, (2) $Bu_2SnL(II)$ complexes that melt and then decompose to give SnO. Mathematical analysis of TG data using Coats-Redfern equation, Horowitz-Metzger equation, and Fuoss method shows that the first order kinetics is applicable in all the complexes except Bu_2SnL-2(II). Kinetic parameters such as the energy and entropy of activation and pre-exponential factor are reported.

Keywords: organotin, Schiff bases, thermal studies

Introduction

A number of metal coordination compounds of Schiff bases have been suggested as models to describe the energy transfer in biological systems [1]. Schiff bases derived from the pyridoxal (vitamin B_6 aldehydes) and various amino acids are believed to be intermediates in biologically important amination processes [2, 3]. Wendlandt [4–7] and Hill [8, 9] studied the thermal properties of metal chelates with different complexing ligands. Studies on thermal decomposition and kinetics of metal chelates with Schiff bases have been done [10–14]. Since there are no reports in the literature dealing with the modes of decomposition of the type of compounds prepared by us [15], we have studied the fate of tin atom in the thermal decomposition of seven dibutyltin compounds. Interpretation and mathematical analysis of these data and evaluation of order of reaction,

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and the energy and entropy of activation, based on the integral method using Coats-Redfern equation [16], the approximation method using the Horowitz-Metzger equation [17] and the Fuoss method [18] are also discussed.

Experimental

Details of synthesis of the complexes, analytical procedures and chemicals used are similar to those described previously [15]. Thermal measurements were carried out using a Stanton-Redcroft STA-780 thermal analyser, which simultaneously records DTA, TG and DTG curves. Sample (10–15 mg) was heated at a rate of 10°C min^{-1} in a platinum crucible to a temperature of around 830°C in dry nitrogen. Alumina was used as reference material, and the chart speed was maintained at 20 cm h^{-1}. X-ray diffraction pattern of the residue obtained in the thermal decomposition of the complexes was recorded on a Philips diffractometer using CuK_α radiation and a nickel filter at 35 kV.

Results and discussion

Structures and stoichiometry of the complexes have been established by the various physicochemical and spectral studies as reported in our previous communication [15] and are represented in Fig. 1(a) and (b).

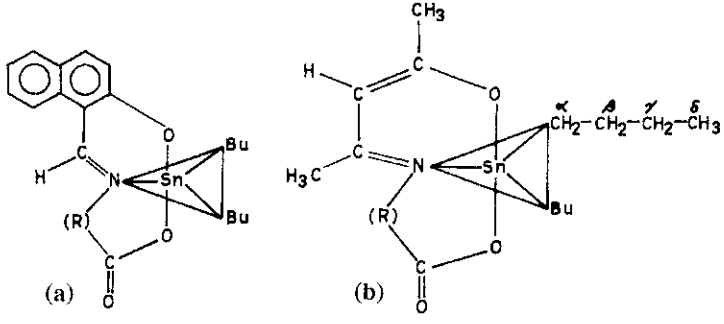

Fig. 1 Structures of (a) $Bu_2SnL(I)$ and (b) $Bu_2SnL(II)$ complexes

where *R*=–CH_2;	Bu_2SnL-1(I)	*R*=–CH_2–CH_2;	Bu_2SnL-2(II)
=>$CHCH_2CH(CH_3)_2$;	Bu_2SnL-4(I)	=>$CHCH(CH_3)_2$);	Bu_2SnL-3(II)
=>$CHCH_2CH_2SCH_3$;	Bu_2SnL-5(I)	=>$CHCH_2CH(CH_3)_2$;	Bu_2SnL-4(II)
=>CHC_6H_5	Bu_2SnL-6(I)		

Typical TG, DTG and DTA curves of all the seven complexes are presented in Figs 2 and 3, and the decomposition temperatures in DTA and DTG along with % mass loss are presented in Table 1.

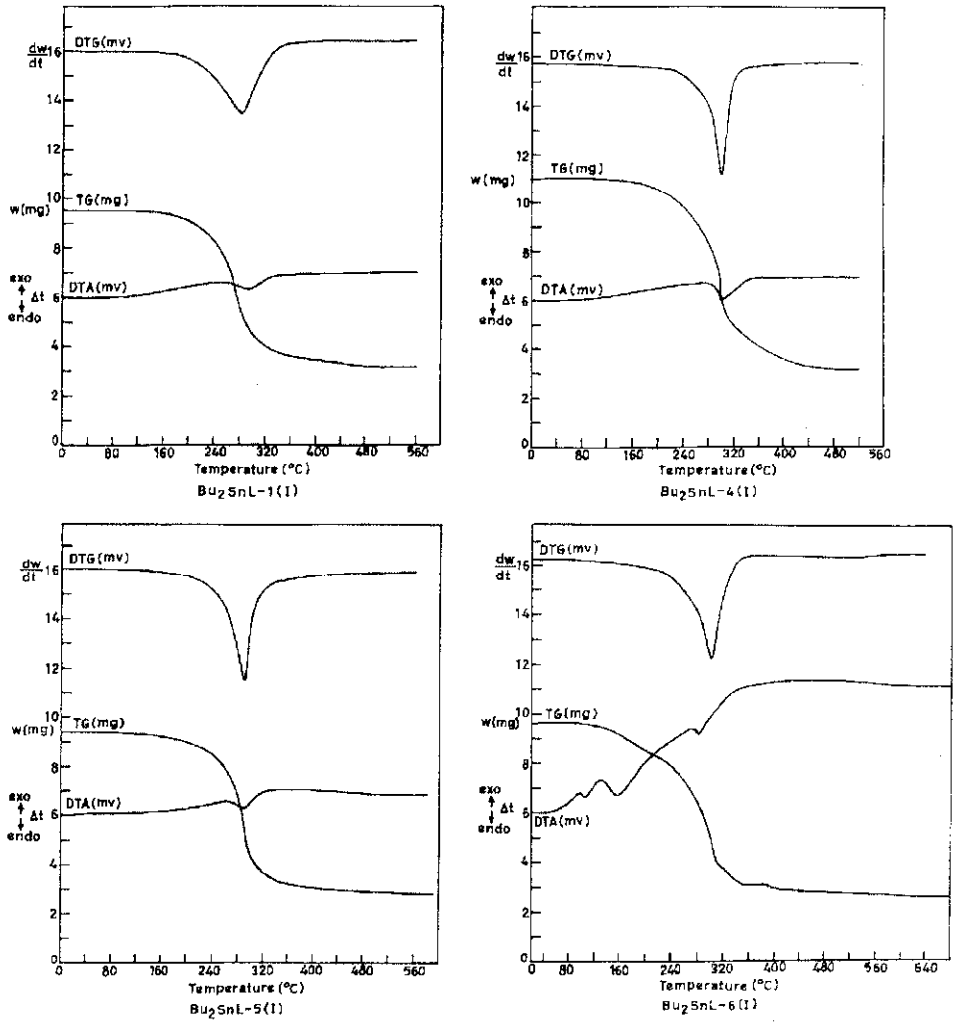

Fig. 2 TG, DTG and DTA curves of $Bu_2SnL(I)$ complexes

Decompositions of Bu_2SnL-1(I), Bu_2SnL-4(I) and Bu_2SnL-5(I) occur in one step between 160–440°C and correspond to the loss of the ligand moiety and organic groups (butyl groups) attached to the tin giving SnO as final residue. Whereas the complex Bu_2SnL-6(I) decomposes in two steps involving the loss of ligand moiety as well as butyl groups attached to the tin giving SnO_2 in first step then SnO.

As is evident from the data compiled in Table 1, the complexes, viz Bu_2SnL-2(II) , Bu_2SnL-3(II) and Bu_2SnL-4(II) decompose after melting in two steps giv-

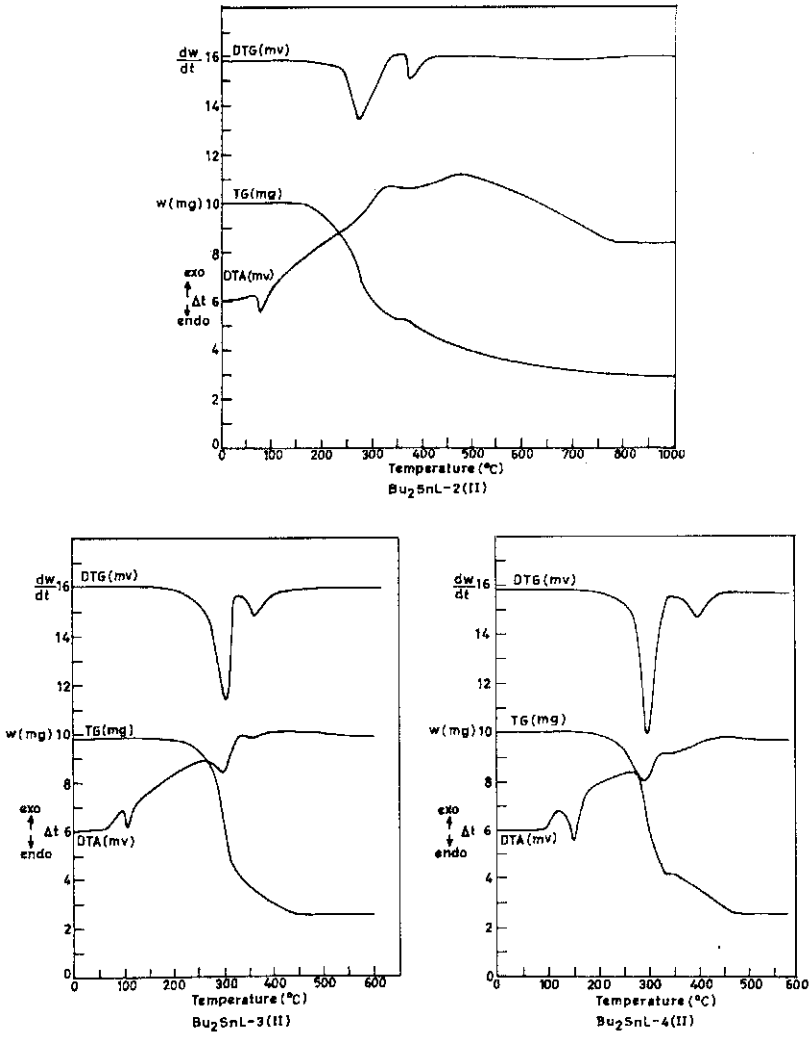

Fig. 3 TG, DTG and DTA curves of Bu_2SnL(II) complexes

ing SnO as final residue. The first step of the decomposition corresponds to the loss of the ligand in Bu_2SnL-2(II), loss of the ligand along with the loss of one butyl group in Bu_2SnL-3(II) and loss of a part of ligand together with one butyl group in Bu_2SnL-4(II). The observed % mass losses in each case correspond to the expected % mass losses and are presented in Table 1.

The TG curves of all the complexes except Bu_2SnL-2(II) were studied in greater detail. The curves in all the complexes exhibited a characteristic, well defined and non-overlapping decomposition pattern. The mass loss consideration and X-ray diffraction pattern of the end product [19] indicated the product to be

SnO in all cases. The relevant portion of the TG curves of Bu_2SnL-1(I), Bu_2SnL-4(I) and Bu_2SnL-5(I), and of the first step of the decomposition of the TG curves of Bu_2SnL-6(I), Bu_2SnL-3(II) and Bu_2SnL-4(II) were drawn on an expanded scale using standard curve sets. Three different methods were used to evaluate kinetic data from the TG traces. The following kinetic data are applicable for the first step of decomposition of the complexes, where the decomposition occurs in two steps. Second step of the decomposition does not follow the first order kinetic and hence kinetic parameters of that step have not been evaluated.

Table 1 Thermal analysis data of Bu_2SnL complexes

Complex (empirical formula)	Step	$T_{range\ TG}$ / °C	$T_{peak\ DTG}$/ °C	$T_{peak\ DTA}$ / (nature of peak) °C	Loss of mass/% *	Loss of mass/% **
Bu_2SnL-1(I)	I	180–410	280	290 (endothermic)	65.29	65.96
$[C_{15}H_{27}NO_3Sn]$				start initially upward		
Bu_2SnL-4(I)	I	160–430	300	302 (endothermic)	69.68	70.91
$[C_{19}H_{35}NO_3Sn]$				start initially upward from 100		
Bu_2SnL-5(I)	I	165–440	290	292 (endothermic)	70.86	70.21
$[C_{18}H_{33}NO_3SSn]$				start initially upward from 114		
Bu_2SnL-6(I)				103 (endothermic)		
$[C_{21}H_{31}NO_3Sn]$	I	130–350	300	157 (endothermic)	67.54	68.75
	II	390–585	–	280 (endothermic) followed by exotherm	3.44	3.65
Bu_2SnL-2(II)				80 (endothermic)	–	–
$[C_{22}H_{29}NO_3Sn]$	I	180–360	271	330 (exothermic)	47.50	48.00
	II	365–775	370	475 (exothermic)	24.09	23.00
Bu_2SnL-3(II)				110 (endothermic)	–	–
$[C_{24}H_{33}NO_3Sn]$	I	205–360	305	300 (endothermic)	61.81	62.44
	II	360–450	360	355 (endothermic) followed by board exotherm upto 530	11.37	11.67
Bu_2SnL-4(II)				145 (endothermic)	–	–
$[C_{25}H_{35}NO_3Sn]$	I	180–331	290	288 (endothermic)	57.42	57.50
	II	344–469	390	followed by board exotherm	16.49	16.50

*theoretical; ** from TG

Table 2 Kinetic data of the thermal decomposition of the complexes

Complexes	Parameters	From Coats-Redfern equation	From Horowitz-Metzger equation	From Fuoss method
Bu_2SnL-1(I)	E^*/kJ mol^{-1}	63	78	62
	A/s^{-1}	$34\cdot10^2$	$11\cdot10^4$	$27\cdot10^2$
	S^*/J K^{-1} mol^{-1}	−183	−153	−184
	G^*/kJ mol^{-1}	159	158	159
	H^*/kJ mol^{-1}	58	73	57
Bu_2SnL-4(I)	E^*/kJ mol^{-1}	55	72	68
	A/s^{-1}	$34\cdot10^1$	$16\cdot10^3$	$69\cdot10^2$
	S^*/J K^{-1} mol^{-1}	−202	−170	−177
	G^*/kJ mol^{-1}	166	165	165
	H^*/kJ mol^{-1}	50	67	63
Bu_2SnL-5(I)	E^*/kJ mol^{-1}	65	82	80
	A/s^{-1}	$45\cdot10^2$	$21\cdot10^4$	$12\cdot10^4$
	S^*/J K^{-1} mol^{-1}	−180	−148	−153
	G^*/kJ mol^{-1}	162	160	161
	H^*/kJ mol^{-1}	60	77	75
Bu_2SnL-6(I)	E^*/kJ mol^{-1}	47	62	52
	A/s^{-1}	$9\cdot10^1$	$17\cdot10^2$	$2\cdot10^2$
	S^*/J K^{-1} mol^{-1}	−213	−189	−208
	G^*/kJ mol^{-1}	165	165	166
	H^*/kJ mol^{-1}	43	57	47
Bu_2SnL-3(II)	E^*/kJ mol^{-1}	100	119	59
	A/s^{-1}	$80\cdot10^5$	$41\cdot10^7$	$7\cdot10^2$
	S^*/J K^{-1} mol^{-1}	−118	−86	−196
	G^*/kJ mol^{-1}	164	164	167
	H^*/kJ mol^{-1}	95	114	54
Bu_2SnL-4(II)	E^*/kJ mol^{-1}	74	94	52
	A/s^{-1}	$36\cdot10^3$	$33\cdot10^5$	$21\cdot10^1$
	S^*/J K^{-1} mol^{-1}	−163	−125	−206
	G^*/kJ mol^{-1}	161	160	163
	H^*/kJ mol^{-1}	70	90	47

The order of decomposition of the tin complexes is obtained by using Horowitz and Metzger equation [17]. The values of C_s for all the six complexes are in the range 0.348–0.376. Therefore, the calculated order in each case shows that the decomposition follows first order kinetics. The values of energy of activation (E^*) and A have been calculated using three different methods, viz Coats-Redfern [16], Horowitz-Metzger [17] and Fuoss [18] methods. Equations (1), (2), (3) and (4) were employed to calculate the activation entropy S^*, the activation enthalpy H^*, the free energy of activation G^* and the specific reaction rate constant K_r [20], respectively.

$$S^* = 2.303\left(\log\frac{Ah}{kT}\right)R \tag{1}$$

$$H^* = E^* - RT \tag{2}$$

$$G^* = H^* - TS^* \tag{3}$$

$$K_r = A\exp(-E^*/RT) \tag{4}$$

where k and h are the Boltzmann and Plank constants, respectively. The data are compiled in Table 2. We have also studied previously the dehydration kinetics of cobalt(II), nickel(II) and copper(II) complexes of Schiff bases derived from salicylaldehyde and glycine [14] and the decomposition kinetics of Ni(II) complexes of Schiff bases derived from *o*-hydroxyacetophenone and valine/methionine [13].

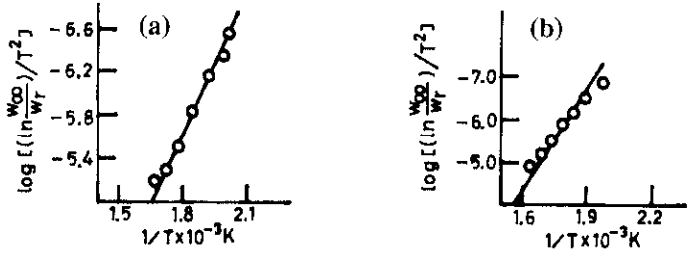

Fig. 4 Coats-Redfern plots for the decomposition of (a) Bu_2SnL-5(I) and (b) Bu_2SnL-3(II) complexes

Dibutyltin complexes of H_2L(I) and H_2L(II) are found to be anhydrous, based on elemental analysis, on the absence of dehydration peaks in DTG and DTA and on the absence of hydroxyl bands in IR spectra. Initial decomposition temperature and inflection temperature have been used to determine thermal stability of these complexes. But as evident from Table 1, Bu_2SnL-2(II), Bu_2SnL-3(II) and Bu_2SnL-4(II) melt at 80, 110, 145°C, respectively, before decomposition sets in. The initial decomposition temperature is frequently used to define the relative

stability of metal chelates [21]. On the basis of experimental data, the relative thermal stability of the seven dibutyltin chelates can be given as:

$$Bu_2SnL\text{-}3(II)<Bu_2SnL\text{-}4(I)<Bu_2SnL\text{-}6(I)<Bu_2SnL\text{-}5(I)<$$
$$Bu_2SnL\text{-}1(I)<Bu_2SnL\text{-}4(II)<Bu_2SnL\text{-}2(II)$$

The values of activation E^* obtained by the three methods are given in Table 2. The values of activation E^* and other kinetic parameters obtained by using Coats-Redfern and Fuoss methods are comparable as compared to those obtained by using Horowitz-Metzger equation, which is an approximate method. The entropies of activation vary from -213 to -86 JK^{-1} mol^{-1}. The negative values of S^* indicate that the reactions are slower than normal.

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