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SOME NEW ORGANOTIN(IV) COMPLEXES WITH KOJIC ACID AND MALTOL
Synthesis, characterization and thermal studies

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Abstract

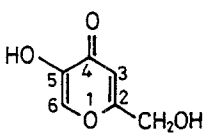
Organotin(IV) complexes of kojic acid and maltol of the type $R_3Sn(L)$ and $R_2Sn(L)Cl$ [$R=C_6H_5CH_2-$, p-$ClC_6H_4CH_2-$; HL=kojic acid, maltol] have been synthesized in anhydrous THF. They were characterized by UV, IR, ^1H NMR, and mass spectral studies. Their activity *vs.* E. coli, S. aureus and P. pyocyanea bacterial strains have been studied and the general order of activity is S. auresu>P. pyocyanea>E. coli. In all the complexes, the ligand acts as bidentate, forming a five membered chelate ring. All the complexes are 1:1 metal ligand complexes. Various thermodynamic parameters have been calculated for the first two decomposition steps using TG/DTA/DSC curves. $(p\text{-}ClC_6H_4CH_2)_3Sn(L)$ complexes have the minimum and $(C_6H_5CH_2)_2Sn(L)Cl$ complexes have the maximum activation energy.

Keywords: kojic acid, maltol, organotin, thermal studies

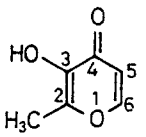
Introduction

Kojic acid and maltol, both are antibiotic substances and are known to inhibit the growth of *E. coli* and *S. aureus* [1, 2]. Since the antibiotic activity of the ligand is altered in the presence of metal ions and the metal complexes of these ligands are of relatively high stability, owing to the formation of five membered chelate ring, it was thought worthwhile to synthesize and characterize some organotin(IV) complexes of kojic acid (a) and maltol (b).

The present work is a sequel to our investigation of metal ion biomolecule interaction [3–7].



a) Kojic acid



b) Maltol

Experimental

The IR spectra were recorded on a Shimadzu IR-435 Spectrophotometer and a Perkin Elmer model-1710. The ^1H NMR spectra were recorded on a Hitachi FT-NMR, R-600 in d_6-DMSO solvent. The UV spectra were recorded on a Beckman DU-64 Spectrometer, in $CHCl_3$. Conductance measurements were carried out

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on Elico Conductivity Bridge (Model CM-821). Mass spectra of the complexes were obtained using a FAB Jeol SX-102 mass Spectrophotometer from CDRI, Lucknow (India). Thermal studies (TG/DTA/DSC curves) were simultaneously recorded on a Rigaku-Thermaflex, in static air at a heating rate of 10°C min^{-1}. A platinum crucible was used with alumina as the reference material. DSC curves were also recorded on the same instrument at a heating rate of 10°C min^{-1} upto 500°C.

Chlorine was determined gravimetrically as silver chloride. Tin was estimated gravimetrically as SnO_2 [8]. The antibacterial activities were evaluated by the cup-plate agar diffusion method [9]. Molecular weights of the compounds were determined by Cottrell's method [10] of boiling point elevation.

Preparation of the complexes

$(C_6H_5CH_2)_3SnCl$, $(C_6H_5CH_2)SnCl_2$, $(p\text{-}ClC_6H_4CH_2)_3SnCl$ and $(p\text{-}ClC_6H_4CH_2)_2SnCl_2$ were synthesized by the method given by Sisido *et al.* [11]. Kojic acid and maltol were procurred from Fluka AG, Switzerland.

The organotin(IV) complexes of kojic acid and maltol were synthesized according to the procedure reported by Bhatia *et al.* [6]. A solution of R_3SnCl or R_2SnCl_2 (0.01 mol) in 25 mol dry THF was added separately to a solution of kojic acid (HL^1, 1.42 g, 0.01 mol) or maltol (HL^2, 1.26 g, 0.01 mol) in 25 ml dry THF. The contents were stirred for about 3 h at room temperature and filtered. The filtrate was evaporated under vacuum to a quarter of its original volume and petroleum ether was added to precipitate the $R_3Sn(L^1)$, $R_3Sn(L^2)$, $R_2Sn(L^1)Cl$, $R_2Sn(L^2)Cl$ complexes. These were filtered, dried and recrystallised from acetone.

Results and discussion

Satisfactory elemental analysis reveal that the complexes are of good purity. The complexes are light yellow in color and are soluble in THF, DMSO, acetone and $CHCl_3$. The analytical data of the complexes along with the yields and melting points are given in Table 1.

From the analytical data, it is clear that organotin(IV) derivatives react with kojic acid or maltol in 1:1 molar proportions. Conductance measurements for these complexes in 10^{-2} *M* nitrobenzene solution are in the range of 0.21 to 0.52 ohm^{-1} cm^2 mol^{-1}, indicating that the complexes are non electrolytes.

The absorption bands at ~1610 cm^{-1} and ~1620 cm^{-1} are assigned to the $\nu_{(C=O)}$ and $\nu_{(C=C)}$ stretching frequencies [12] respectively, in the free ligand. Both bands undergo batho chromic shifts of ~20–70 cm^{-1} on complexation, indicating the involvement of the carbonyl group in complexation. The $\nu_{(O-H)}$ phenolic stretching frequency, which appears at 3180 cm^{-1} in kojic acid and at 3170 cm^{-1} in maltol disappears on complexation. Kojic acid also shows an additional peak at 3550 cm^{-1}, which is due to (O–H) alcoholic stretching mode. This peak remains almost unaltered on complexation.

In the far IR region, the bands at ~440, ~340 and ~310 cm^{-1} correspond to O–Sn–O chelate bond [16]. The $\nu_{(Sn-Cl)}$ is observed in the range 270–290 cm^{-1}.

Table 1 Analytical data of complexes

Complex	Empirical formula	Mol. wt. found/(calc.)	Analysis % found/(calc.)				Yield/ %	*m.p.*/ °C
			C	H	Cl	Sn		
$(C_6H_5CH_2)_3Sn(L^1)$	$C_{27}H_{26}SnO_4$	531.48	60.21	4.39	–	21.62	67	161
		(533.19)	(60.82)	(4.91)	–	(22.26)		
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)$	$C_{27}H_{23}O_4SnCl_3$	634.76	50.79	3.01	16.21	18.09	58	165
		(635.92)	(50.99)	(3.64)	(16.63)	(18.66)		
$(C_6H_5CH_2)_2Sn(L^1)Cl$	$C_{20}H_{19}O_4SnCl$	475.21	49.91	3.84	9.96	24.21	64	170
		(477.31)	(50.32)	(4.01)	(7.38)	(24.86)		
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl$	$C_{20}H_{17}O_4SnCl_3$	544.29	43.62	2.56	19.01	21.20	54	162
		(545.80)	(44.01)	(3.13)	(19.37)	(21.74)		
$(C_6H_5CH_2)_3Sn(L^2)$	$C_{27}H_{26}SnO_3$	516.91	61.87	4.08	–	22.24	68	169
		(517.14)	(62.70)	(5.03)	–	(22.95)		
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)$	$C_{27}H_{23}O_3SnCl_3$	616.79	51.98	3.32	16.44	18.92	54	164
		(619.92)	(52.31)	(3.73)	(17.06)	(19.14)		
$(C_6H_5CH_2)_2Sn(L^2)Cl$	$C_{20}H_{19}O_3SnCl$	460.92	51.86	3.99	7.21	25.21	60	171
		(461.31)	(52.07)	(4.15)	(7.64)	(25.72)		
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^2)Cl$	$C_{20}H_{17}O_3SnCl_3$	529.04	44.98	2.92	19.21	22.19	57	163
		(529.80)	(45.34)	(3.23)	(19.99)	(22.40)		

All facts indicate that kojic acid and maltol, both are co-ordinated to the metal ion through the oxygen atom of the –OH (phenolic) group, forming a five membered chelate structures as shown in Fig. 1.

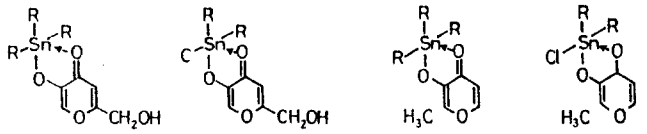


Fig. 1 I (a), I (b)=kojic acid (HL^1) complexes; II (a), II (b)=maltol (HL^2) complexes

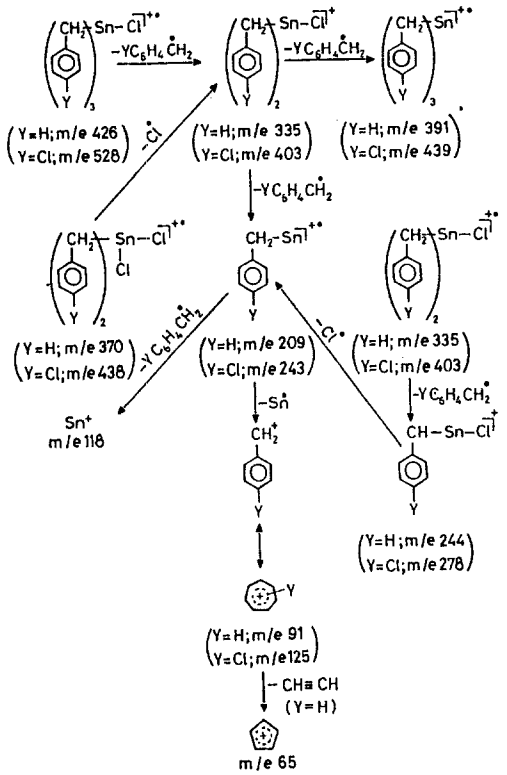
In the electronic spectra the band corresponding to $\pi \rightarrow \pi^*$ transition of the carbonyl group and pyran ring appears at ~215 nm and ~270 nm; respectively, in the free ligands. The band corresponding to the C=O group shifts to longer wavelength on complexation, showing the involvement of the C=O group in complexation, in both the ligands. The O → Sn charge transfer [17, 18] band is observed in the region 325 nm to 350 nm in the complexes.

The ^{1}H NMR spectra of kojic acid gives the following signals: δ 8.6–8.9 (br,1H, phenolic-OH), δ 2.6–2.7 (s, 1H, alcoholic-OH); δ 4.4–4.5 (s, 2H, CH_2 at C2); δ 6.4 (s, 1H, H3) and δ 7.80 (s, 1H, H6). On complexation, peaks were observed at the following values: the peak corresponding to phenolic-OH disappears; δ 2.6–2.7 (s, 1H, alcoholic-OH); δ 4.4 –4.5 (s, 2H, CH_2 at C2); δ 6.6–6.7 (s, 1H, H3); δ 8.0–8.1 (s, 1H, H6). The downfield shift of the signals for H3 and H6 are attributed to the involvement of the carbonyl group at C4 and phenolic group at C5 in complexation. The ^{1}H NMR spectra of maltol gives the following signals: δ 2.8 (s, 3H, CH_3 at C2); δ 6.2 (d, 1H, H5); δ 7.8 (d, 1H, H6); δ 8.6–8.8 (br, –OH at C-3). On complexation, the peaks corresponding to phenolic-OH disappears and other peaks shows following shifts: δ 2.8–2.9 (s, 3H, CH_3 at C2); δ 6.5–6.6 (d, 1H, H5); δ 8.0–8.1 (d, 1H, H6). The downfield shifts of the signals, especially of the signal due to H5, on complexation indicates the involvement of the carbonyl group at C4 in complexation. Along with these peaks, additional peaks in the region δ 7.0–7.5 (Ar-H) and δ 3.3–3.6 (s, CH_2-group), corresponding to the *R* moiety, also appear in the ^{1}H NMR spectra of the complexes.

The carbonium ion R^+, constitutes the base peak in the mass spectra of all the complexes. Hence, for the complexes with R=$C_6H_5CH_2$–, *p*-$ClC_6H_4CH_2$–, the base peaks are at *m/e* 91 (tropylium ion) and *m/e* 125 (chlorotropylium ion) respectively. The fragmentation pattern for the *R* moiety is given in Scheme 1.

The mass spectra of the complexes showed a peak at *m/e* 141, corresponding to the kojic acid. This fragment cleaves by pathways, (a), (b) and (c), as shown in scheme II. In pathway (a), the acid fragment further cleaves to give peaks at *m/e* 111 and 83. In pathway (b), the peak at *m/e* 141 cleaves to give peaks at *m/e* 85 and 57. In pathway (c), the kojic acid fragment (*m/e* 141) further cleaves to give the fragments at *m/e* 100, 70, 65, 42.

The mass spectra of the maltol complexes show a peak at *m/e* 125, corresponding to the maltol molecular ion, which further cleaves by pathways (a), (b) and (c),



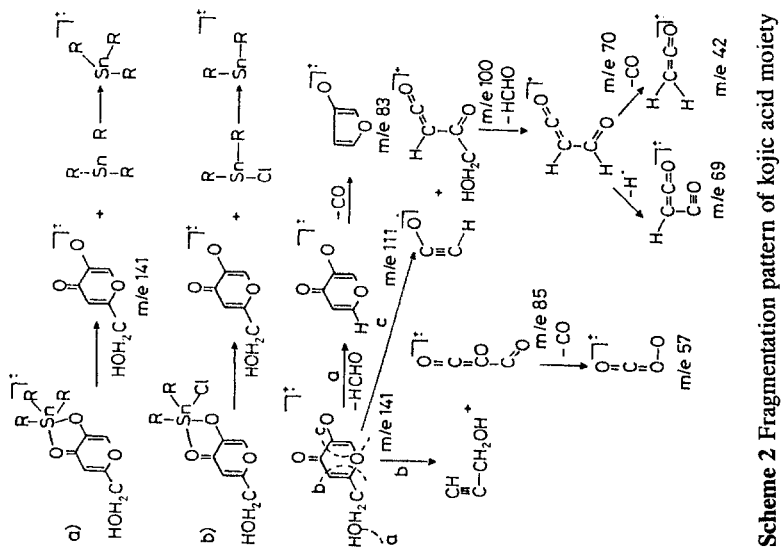
Scheme 1 Fragmentation pattern of *R* moiety

as shown in Scheme 3. In pathway (a), the molecular ion at *m/e* 125 gives peaks at *m/e* 99 and 71. In pathway (b), peaks at *m/e* 70 and 69 are obtained. In pathway (c), the molecular ion (*m/e* 125) gives a peak at *m/e* 97, after losing a CO group.

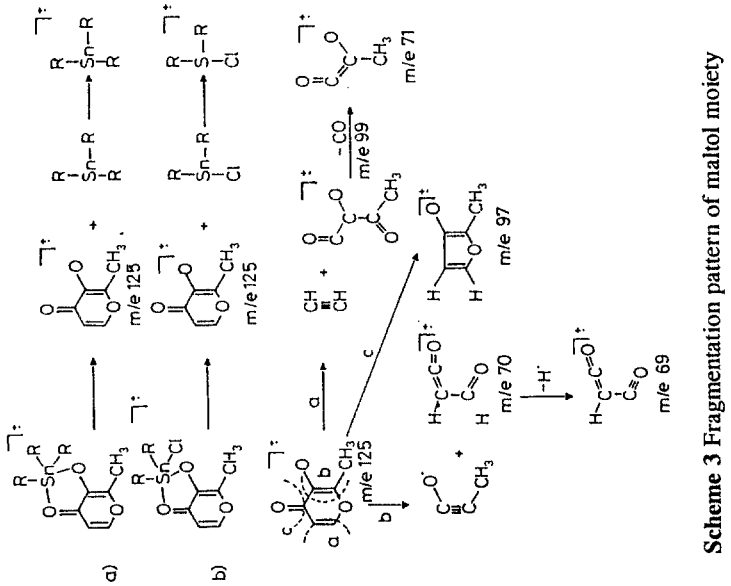
The metal complexes were tested *vs. E. coli, P. pyocyanea* and *S. aureus* bacterial strains, using the respective ligands as the standard for comparing the activities. The samples were screened at three concentrations (25, 50 and 100 μg cm^{-3}) in DMF. The inhibitory power of the metal complexes was greater than that of the control. The general order of activity *vs.* the three microorganisms is *S. aureus>P. pyocyanea>E. coli* and the maltol complexes show greater inhibition than the kojic acid complexes. $(C_6H_5CH_2)_3Sn(L^2)$ complex is most active at all the three concentrations and *vs.* the three microorganisms. The data is given in Table 4.

Thermal studies

Thermogravimetric (TG) studies have been carried out for all the complexes as shown in Fig. 2 and Table 2. The complexes of the type $R_3Sn(L)$ (*HL*=kojic acid, maltol) decompose in two steps. The first step (150–450°C) involves the loss of *R* groups, and the second step (550–700°C) corresponds to the formation of SnO_2.



Scheme 2 Fragmentation pattern of kojic acid moiety



Scheme 3 Fragmentation pattern of maltol moiety

Table 2 Thermodynamic and kinetic parameters

Complex	Step no.	T_{range}/ °C	Coats-Redfern method		Horowitz-Metzger method		DTA		DSC
			E_a / kJ mol^{-1}	Δs^+ / J K^{-1}mol^{-1}	E_a / kJ mol^{-1}	Δs^+ / J K^{-1}mol^{-1}	Thermal effect	ΔH / J g^{-1}	ΔH / J g^{-1}
$(C_6H_5CH_2)_3Sn(L^1)$	1	220–450	53.19	43.37	54.23	41.39	Exo.	–25.90	–26.41
	2	580–700	83.76	51.00	77.20	58.95	Endo.	76.62	–
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)$	1	220–450	47.86	48.62	52.60	39.18	Exo.	–17.48	–17.01
	2	600–700	119.66	76.57	121.10	75.07	Endo.	120.12	–
$(C_6H_5CH_2)_2Sn(L^1)Cl$	1	170–400	57.44	64.72	60.46	68.58	Exo.	–25.35	–26.61
	2	500–620	95.73	63.75	101.02	67.23	Exo.	–83.38	–
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl$	1	200–415	57.44	81.95	58.55	89.80	Exo.	–29.42	–27.42
	2	550–710	100.52	129.40	117.45	109.15	Exo.	–135.62	–
$(C_6H_5CH_2)_3Sn(L^2)$	1	220–400	43.51	8.14	49.55	9.90	Exo.	–45.36	–43.31
	2	580–680	229.76	43.79	233.02	44.96	Endo.	86.55	–
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)$	1	230–430	41.62	7.01	45.32	8.12	Exo.	–44.72	–44.09
	2	620–710	153.77	17.14	136.21	16.17	Endo.	124.18	–
$(C_6H_5CH_2)_2Sn(L^2)Cl$	1	185–350	48.79	10.21	48.79	10.61	Exo.	–27.43	–29.46
	2	460–600	210.61	32.31	224.79	33.09	Exo.	–103.12	–
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^2)Cl$	1	180–360	42.54	9.89	45.04	9.53	Exo.	–61.76	–62.71
	2	480–590	220.19	32.40	237.07	34.93	Exo.	–58.85	–

The complexes of the type $R_2Sn(L)Cl$, decompose in three steps. The first step (150–400°C) corresponds to the loss of *R* groups, the second step (420–600°C) involves the loss of Cl (for maltol complexes) or the kojic acid moiety (for kojic acid

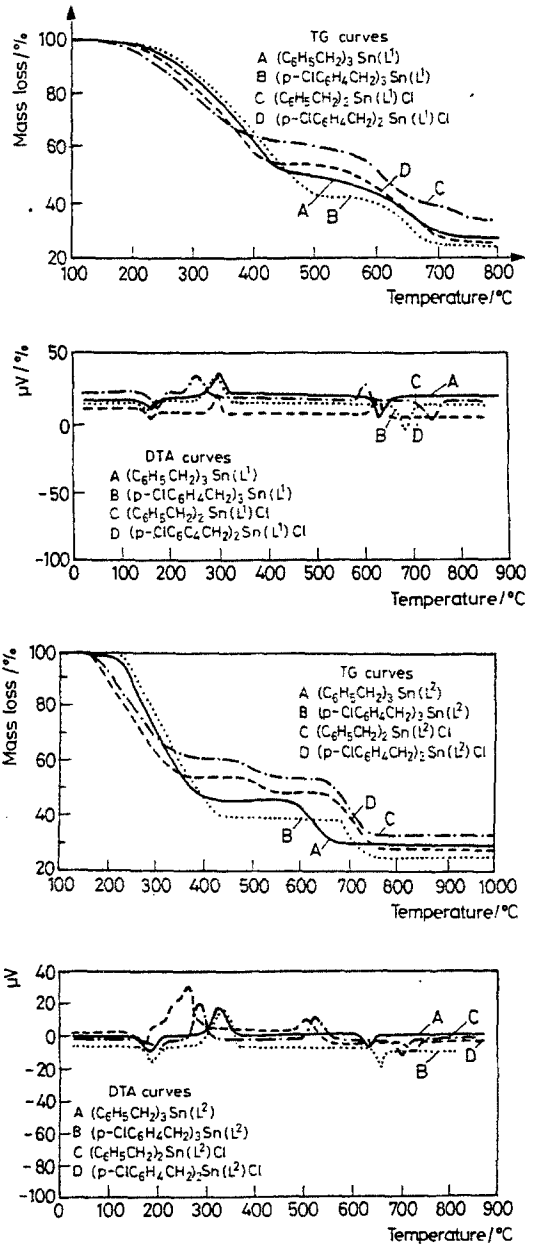


Fig. 2 I=TG for kojic acid complexes, II=DTA for kojic acid complexes, III=TG for maltol complexes, IV=DTA for maltol complexes

Table 3 Mass loss data of complexes

Complex	Step no.	T_{range}/ °C	Mass loss/% found	Mass loss/% (calc.)	Nature of loss
$(C_6H_5CH_2)_3Sn(L^1)$	1	220–450	50.9	(51.27)	Loss of 3 benzyl groups
	2	580–700	70.1	(71.85)	Formation of SnO_2
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)$	1	220–450	58.5	(59.14)	Loss of 3 *p*-chloro benzyl groups
	2	600–700	76.0	(76.40)	Formation of SnO_2
$(C_6H_5CH_2)_2Sn(L^1)Cl$	1	170–400	37.0	(38.18)	Loss of 2 benzyl groups
	2	500–620	64.0	(64.74)	Loss of kojic acid moiety
	3	710–770	67.0	(68.56)	Formation of SnO_2
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl$	1	200–415	44.5	(45.94)	Loss of 2 *p*-chloro benzyl groups
	2	550–710	70.0	(71.79)	Loss of kojic acid moiety
	3	720–760	72.0	(72.50)	Formation of SnO_2
$(C_6H_5CH_2)_3Sn(L^2)$	1	220–400	52.0	(52.86)	Loss of 3 benzyl groups
	2	580–680	69.9	(70.98)	Formation of SnO_2
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)$	1	230–430	60.0	(60.67)	Loss of 3 *p*-chloro benzyl groups
	2	620–770	74.0	(75.79)	Formation of SnO_2
$(C_6H_5CH_2)_2Sn(L^2)Cl$	1	185–350	38.7	(39.51)	Loss of 2 benzyl groups
	2	460–600	46.0	(47.15)	Loss of chlorine
	3	660–750	66.0	(67.47)	Formation of SnO_2
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^2)Cl$	1	180–360	46.0	(47.33)	Loss of 2 *p*-chloro benzyl groups
	2	480–590	52.0	(53.98)	Loss of two chlorines
	3	660–770	71.0	(71.67)	Formation of SnO_2

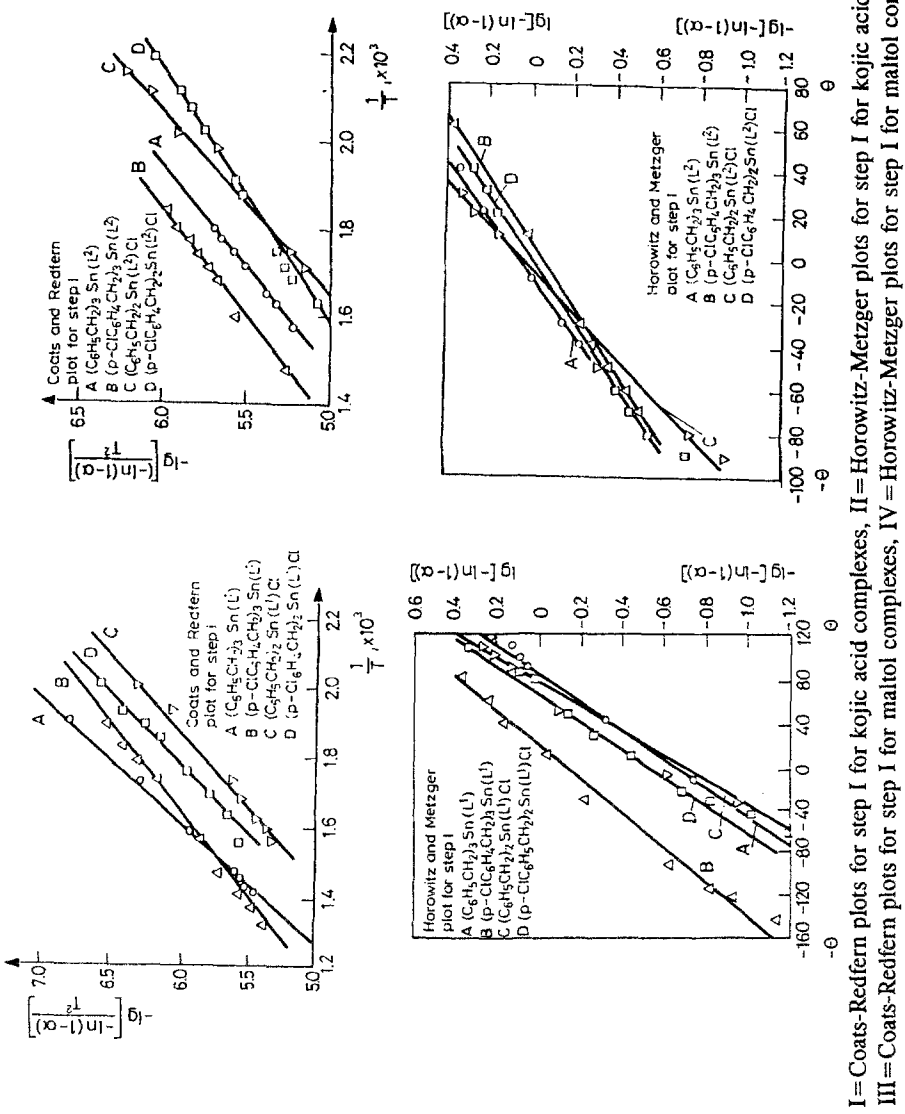


Fig. 3 I = Coats-Redfern plots for step I for kojic acid complexes, II = Horowitz-Metzger plots for step I for kojic acid complexes, III = Coats-Redfern plots for step I for maltol complexes, IV = Horowitz-Metzger plots for step I for maltol complexes

complexes) and the third step (700–800°C) corresponds to the formation of SnO_2. The order (n) and activation energy (E_a) have been elucidated for first two decomposition steps using both, the Coats-Redfern [19] and Horowitz-Metzger [20] methods (Figs 3 and 4) and the values are in close agreement. The order of reaction in each case is one. The mass loss data of the complexes is given in Table 3.

$\Delta S^{\neq}$ (entropy of activation) and ΔH (heat of reaction) have been calculated, using the TG [23] and DTA curves respectively [21, 22]. The ΔH values of the first decomposition step calculated from the DTA curve have also been compared with the ΔH values obtained from differential scanning calorimetry (DSC) curves and the values have been found in good agreement. On the basis of the above data, following the conclusions have been drawn:

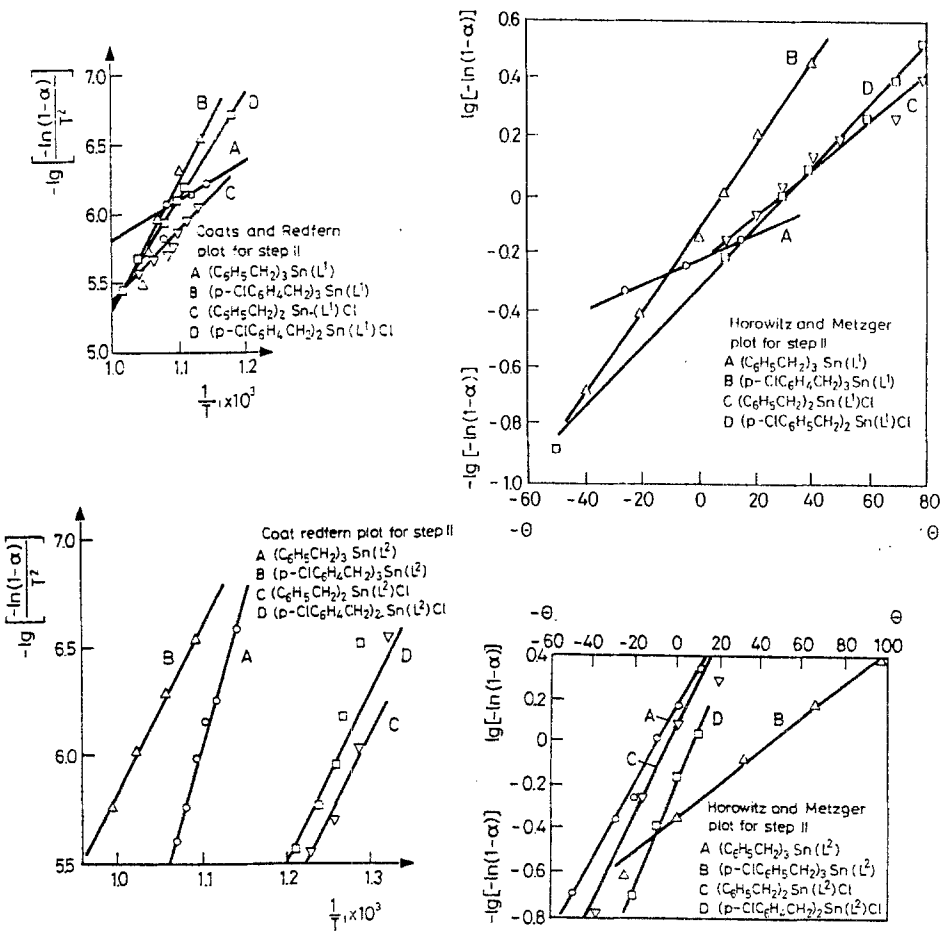


Fig. 4 I = Coats-Redfern plots for step II for kojic acid complexes, II = Horowitz-Metzger plots for step II for kojic acid complexes, III = Coats-Redfern plots for step II for maltol complexes, IV = Horowitz-Metzger plots for step II for maltol complexes

Table 4 Antibacterial activity of kojic acid (HL^1) and maltol (HL^2) complexes

Compound	*E. coli*			*P. pyocyanea*			*S. aureus*		
	25	50	100	25	50	100	25	50	100
	$\mu g\ cm^{-3}$			$\mu g\ cm^{-3}$			$\mu g\ cm^{-3}$		
kojic acid	–	+	+	+	+	+++	+	+++	++++
$(C_6H_5CH_2)_3Sn(L^1)$	–	+	+	+	+	+++	+	+++	++++
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)$	–	+	+	+	+	+++	+++	+++	++++
$(C_6H_5CH_2)_2Sn(L^1)Cl$	+	+	+	+	+	+	+++	+++	+++
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl$	+	+	+	+	+	+++	+++	+++	++++
maltol	+	+	+	+	+	+	+	+++	+++
$(C_6H_5CH_2)_3Sn(L^2)$	+	+	+++	+	+++	++++	+++	++++	+++++
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)$	+	+	+	+	+	+++	+	++++	+++
$(C_6H_5CH_2)_2Sn(L^2)Cl$	+	+	+	+	+++	++++	+++	+++	++++
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^2)Cl$	–	–	+	+	+	+	+++	+++	++++

1) the Sn–R bond is weaker than Sn–Cl bond and hence the Sn–R bond breaks first;

2) the activation energy value for step 1 is lower for complexes of the type $R_3Sn(L)$ as compare to that of the complexes of type $R_2Sn(L)Cl$ ($R=C_6H_5CH_2-$, p-$ClC_6H_4CH_2-$), because of greater steric hinderance in the $R_3Sn(L)$ complexes;

3) the complexes with $R=p$-$ClC_6H_4CH_2-$ have lower E_a value for the 1 step as compared to the complexes with same number of R groups, but $R=C_6H_5CH_2-$ because the electron withdrawing effect of the chlorine makes the R–Sn bond weaker and facilitates its thermal degradation. Thus (p-$ClC_6H_4CH_2)_3Sn(L)$ complexes have the minimum E_a and $(C_6H_5CH_2)_2Sn(L)Cl$ complexes have the maximum E_a.

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