THERMAL INVESTIGATIONS ON ARYLMERCURY(II) COMPLEXES OF KOJIC ACID AND MALTOL
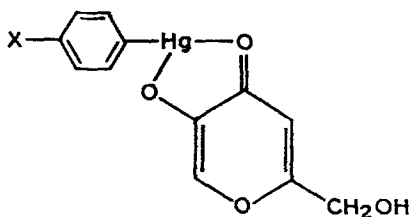
J. Kaur* and G. S. Sodhi**

Department of Chemistry, University of Delhi, Delhi-110007
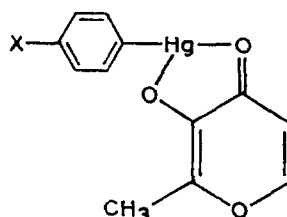**Department of Chemistry, S. G. T. B. Khalsa College, University of Delhi, Delhi-110007, India

Abstract

Arylmercury(II) derivatives of kojic acid and maltol of the type p-$XC_6H_4HgL^1$ (I) and p-$XC_6H_4HgL^2$ (II) [HL^1=kojic acid, HL^2=maltol; X=M, MO, NO_2] have been synthesised. IR spectral studies indicate that both the ligands act as bidentate groups, bonding to the mercury(II) ion through phenolic and carbonyl oxygens. From TG curves, the order and activation energy of the thermal decomposition reaction have been elucidated. The variation of the activation energy has been correlated with the nature of the substituents on the phenyl ring. The heat of reaction has been elucidated from differential scanning calorimetric studies. The fragmentation pattern has been analysed on the basis of mass spectra.

(I)   (II)

X = Me, MeO, NO_2

Keywords: complexes

---

* Present address: Department of Chemistry, S. G. T. B. Khalsa College, University of Delhi, Delhi-110007 India.

Introduction

The interest in the thermal studies on metal complexes of kojic acid and maltol has been stimulated due to the fact that these compounds possess relatively high thermal stability, owing to the formation of a five membered chelate ring [1, 2]. In this paper we report the results of TG and DSC studies for some arylmercury(II) complexes of kojic acid and maltol.

Experimental

A RIGAKU 8150 instrument was used for recording TG curves upto 1273 K and DSC curves upto 673 K in air atmosphere, at a heating rate of 15 deg·min^{-1}. The crystalline samples (ca. 35 mg) were placed in platinum crucible. For DSC studies alumina was used as the reference. A Shimadzu spectrophotometer IR-435 and a Jeol JMX DX-303 spectrometer were used for recording IR and mass spectra respectively.

Kojic acid and maltol were procured from Fluka, AG, Switzerland and used without further purification. The arylmercury(II) chlorides, p-XC$_6$H$_4$HgCl (X=M, MO, NO$_2$) were synthesised by the method of Nesmeyanov et $al.$[3].

A solution of p-XC$_6$H$_4$HgCl (0.01 mol) in 25 ml DMF was slowly added to a solution of kojic acid (0.01 mol) in 25 ml DMF at a pH of 8–9. The contents were stirred for 6 h at 50°C and filtered. The filtrate was slowly added to crushed ice with vigorous stirring. The precipitates so obtained were washed successively with hot water and benzene. The resulting product was recrystallised from THF. The maltol complexes were prepared by following a similar method.

The IR spectra of kojic acid and maltol showed an intense band at 1650 cm^{-1} [4]. On complexation, this frequency was reduced by ca. 50 cm^{-1}, indicating that the carbonyl group chelated to the mercury(II) ion. The ν(C=C) stretching frequency observed at 1580 and 1610 cm^{-1} for kojic acid and maltol respectively, was shifted to ca. 1560 cm^{-1} in the complexes, due to the formation of coordinate bonds to the metal ion [5].

Results and discussion

The TG curves of kojic acid and maltol complexes are presented in Figs 1 and 2 respectively. The corresponding DSC curves are depicted in Figs 3 and 4. The decomposition pattern of the complexes is shown in Scheme I.

From TG curves, the weight loss accompanying the thermal degradation of the complexes has been calculated. In each case, the theoretical as well as the calculated mass change corresponded to the formation of mercury(II) oxide. Beyond ca. 750 K, HgO slowly volatilised, leaving the crucible of the thermo-
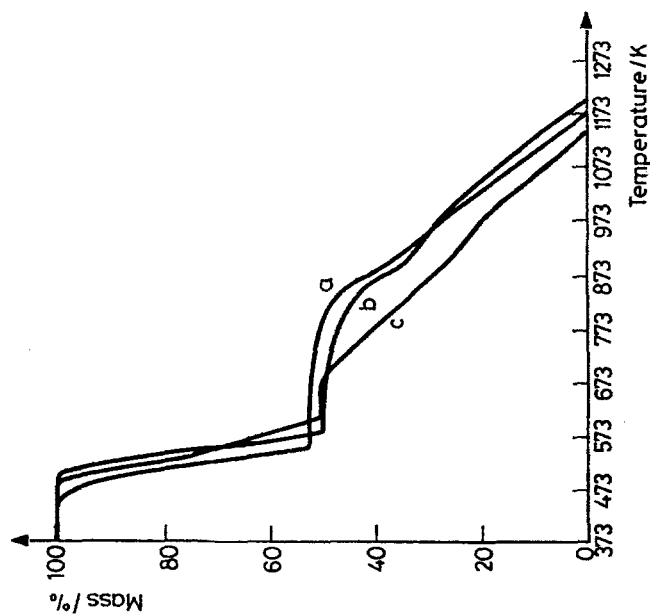
Fig. 2 TG curves of maltol complexes: (A) p-MC$_6$H$_4$HgL^2; (B) p-MOC$_6$H$_4$HgL^2; (C) p-NO$_2$C$_6$H$_4$HgL^2
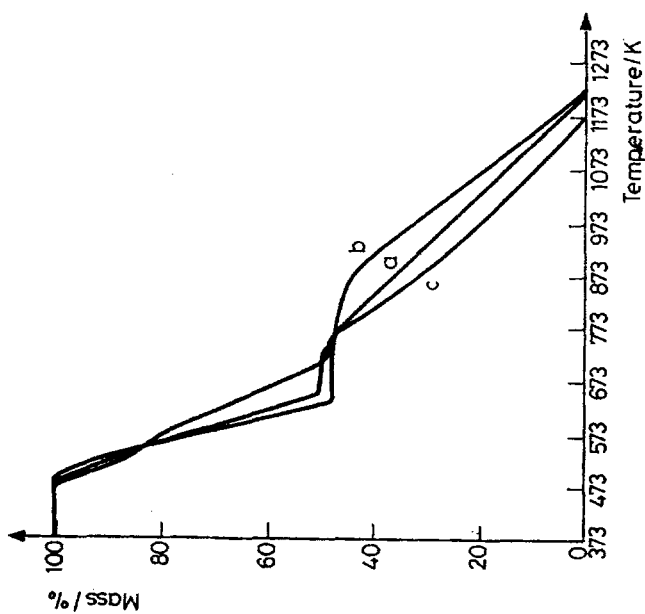
Fig. 1 TG curves of kojic acid complexes: (A) p-MC$_6$H$_4$HgL^1; (B) p-MOC$_6$H$_4$HgL^1; (C) p-NO$_2$C$_6$H$_4$HgL^1

Kojic Acid Complexes

$$CH_3C_6H_4Hg(C_6H_5O_4)+7O_2 \xrightarrow{478-658\ K} HgO\ +6H_2O\ +13CO_2$$
(I; X=M)

$$CH_3C_6H_4Hg(C_6H_5O_4)+14O_2 \xrightarrow{493-638\ K} HgO\ +6H_2O\ +13CO_2$$
(I; X=MO)

$$2NO_2C_6H_4Hg(C_6H_5O_4)+12.5O_2 \xrightarrow{425-723\ K} 2HgO\ +9H_2O\ +$$
$$24CO_2\ +2NO_2$$
(I; X=NO$_2$)

Maltol Complexes

$$CH_3C_6H_4Hg(C_6H_5O_3)+15O_2 \xrightarrow{468-557\ K} HgO\ +6H_2O\ +13CO_2$$
(II; X=M)

$$CH_3OC_6H_4Hg(C_6H_5O_3)+7O_2 \xrightarrow{498-579\ K} HgO\ +6H_2O\ +13CO_2$$
(II; X=MO)

$$2NO_2C_6H_4Hg(C_6H_5O_3)+13O_2 \xrightarrow{490-608\ K} 2HgO\ +9H_2O\ +$$
$$24CO_2\ +2NO_2$$
(II; X=NO$_2$)
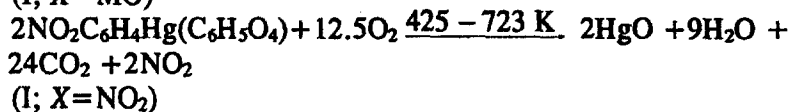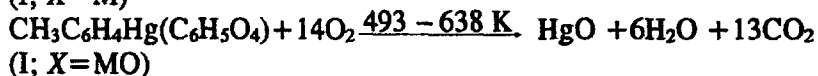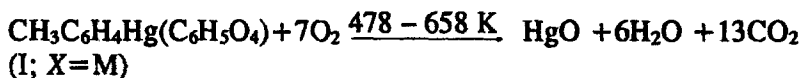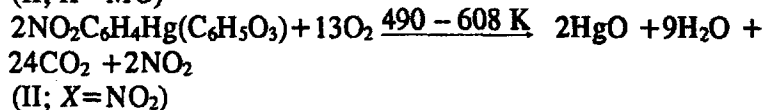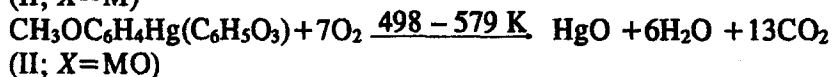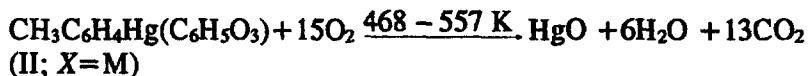
Scheme I. Decomposition pattern of the complexes
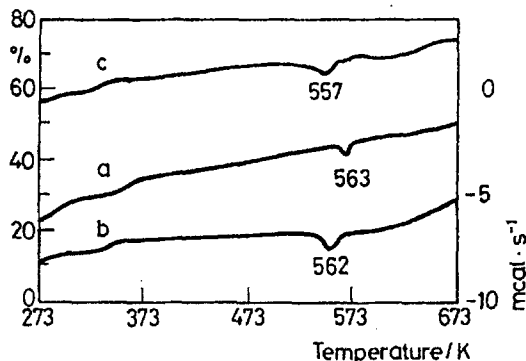
Fig. 3 DSC curves of kojic acid complexes: (A) p-MC$_6$H$_4$HgL^1; (B) p-MOC$_6$H$_4$HgL^1;
(C) p-NO$_2$C$_6$H$_4$HgL^1

balance empty. The DSC profile showed, in each case, an endothermic thermal effect corresponding to the decomposition of the complex to HgO. Thermal data are presented in Table 1.

From the TG curves, the order (n) and activation energy (E_a) of the thermal decomposition reaction have been obtained by the method of Coats and Redfern [6]. The linearisation curves of kojic acid and maltol complexes are shown in Figs 5 and 6 respectively.

Table 1 Thermal data

Compound	TG			Thermal effect	DSC	
	T_{range}/K	n	E_a/kcal mol^{-1}		T_{max}/K	ΔH/cal g^{-1}
p-MC$_6$H$_4$HgL^1	478–658	1	6.53	Endothermic	563	25.17
p-MOC$_6$H$_4$HgL^1	493–638	1	7.62	Endothermic	562	28.62
p-NO$_2$C$_6$H$_4$HgL^1	475–723	1	5.72	Endothermic	557	35.75
p-MC$_6$H$_4$HgL^2	468–557	1	10.36	Endothermic	498	60.26
p-MOC$_6$H$_4$HgL^2	498–579	1	21.72	Endothermic	522	71.72
p-NO$_2$C$_6$H$_4$HgL^2	490–608	1	5.00	Endothermic	558	36.45

The order of reaction in each case is unity. A comparison of the activation energy data for each series of complexes reveal that the p-nitrophenylmercury(II) derivative had the lowest value of E_a. This may be explained on the basis of the electron withdrawing effect of the nitro group, which causes the
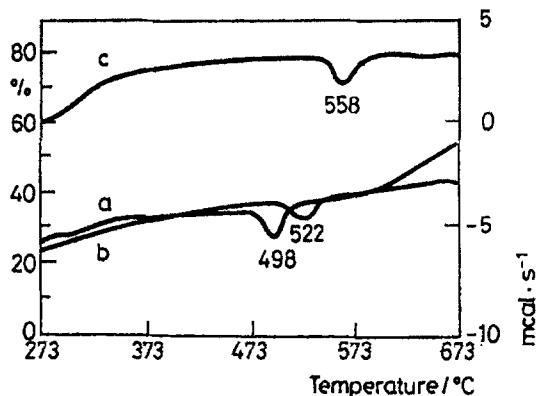

Fig. 4 DSC curves of maltol complexes: (A) p-MC$_6$H$_4$HgL^2; (B) p-MOC$_6$H$_4$HgL^2; (C) p-NO$_2$C$_6$H$_4$HgL^2
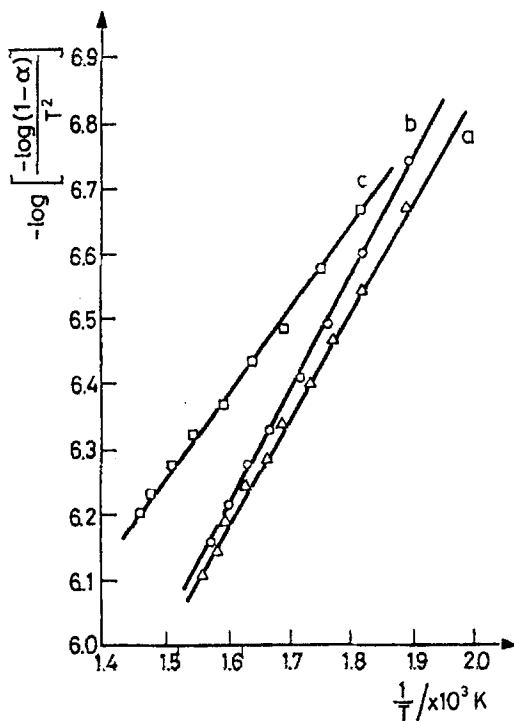
Fig. 5 Linearisation curves of kojic acid complexes: (A) p-MC$_6$H$_4$HgL^1; (B) p-MOC$_6$H$_4$HgL^1; (C) p-NO$_2$C$_6$H$_4$HgL^1
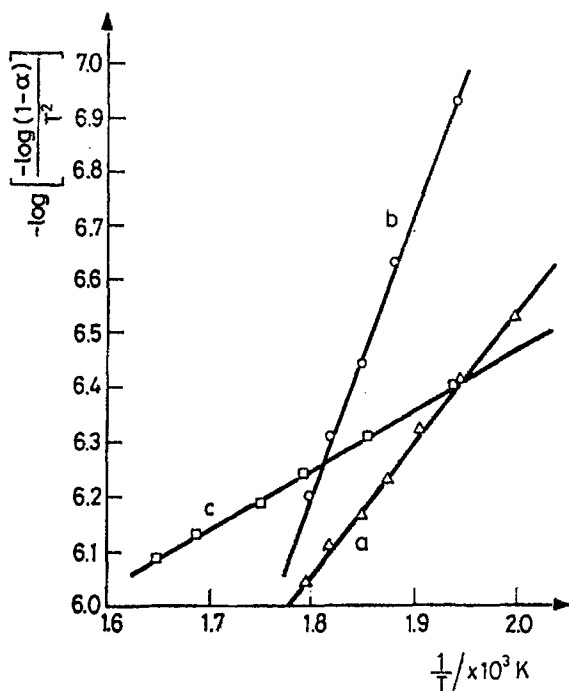
Fig. 6 Linearisation curves of maltol complexes: (A) p-MC$_6$H$_4$HgL^2; (B) p-MOC$_6$H$_4$HgL^2; (C) p-NO$_2$C$_6$H$_4$HgL^2

weakening of the metal-ligand bond, consequently making thermal degradation relatively easy. In case of p-methylphenylmercury(II) analogue, the methyl group was of electron releasing type and the metal-ligand bond was strengthened, which subsequently resulted in higher E_a value for thermal reaction. As the methoxy group had a greater electron donating character than the methyl group, the p-methoxyphenylmercury(II) compound had the highest value of E_a. Thus for any one of the ligand, the activation energy varied in the order, $X=MO>M>NO_2$.

That the XC$_6$H$_4$–Hg bond cleavage was involved in the pyrolysis of complexes was also evidenced from the mass spectra. The carbonium ion, XC$_6$H$_4^+$, constituted the base peak in each case. Thus, the peaks at m/e 91, 107 and 122 corresponded to the formation of MC$_6$H$_4^+$, MOC$_6$H$_4^+$ and NO$_2$C$_6$H$_4^+$ fragments respectively.

The TG data are supplemented by DSC studies. The heat of reaction (ΔH) has been elucidated from the DSC curves.

* * *

References

1 N. K. Dutt and U. U. M. Sarma, J. Inorg. Nucl. Chem., 37 (1975) 1801.
2 C. Gerard, Bull. Soc. Chim. Fr., (1979) 451.
3 A. N. Nesmeyanov, L. G. Makarova and I. V. Polovyanyuk, J. Gen. Chem., 35 (1965) 682.
4 A. R. Katritzky and R. A. Jones, Spectrochim. Acta, 17 (1961) 64.
5 R. C. Agarwal, S. P. Gupta and R. K. Rastogi, J. Inorg. Nucl. Chem., 36 (1974) 208.
6 A. W. Coats and J. P. Redfern, Nature (London), 201 (1964) 68.