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THERMAL STUDIES ON ORGANOMERCURY(II) COMPLEXES OF KOJIC ACID AND MALTOL

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ABSTRACT

Thermal studies on organomercury(II) derivatives of Kojic acid and maltol of the type $RHgL^1$ and $RHgL^2$ [R = phenyl (C_6H_5), p-hydroxyphenyl (p-HOC_6H_4), p-acetoxyphenyl (p-$AcOC_6H_4$); HL^1 = Kojic acid, HL^2 = maltol] have been carried out. From thermogravimetric (TG) curves, the order, activation energy and apparent activation entropy of the thermal decomposition reaction have been elucidated. The variation of activation energy has been correlated with the nature of the substituent on the phenyl ring. The heat of reaction has been determined from differential scanning calorimetric (DSC) studies.

INTRODUCTION

The metal complexes of Kojic acid and maltol are of relatively high stability, owing to the formation of the five membered chelate ring. The thermal stability of quite a few complexes has, therefore, been briefly investigated [1,2]. In this communication we report the results of TG and DSC studies of some organomercury(II) complexes of Kojic acid and maltol. This follows from our previous investigation on the thermal behaviour of metal ion - biomolecule systems [3,4].

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TABLE 1

Thermal data

Complex	TG					DSC		
	Temp.range K	Wt. loss obs.(calc.)%	n	E_a KJ mol^{-1}	$\Delta S^{\neq}$ J deg^{-1}mol^{-1}	Thermal effect	T_{max} K	ΔH KJ mol^{-1}
$C_6H_5HgL^1$	473-673	58.6(54.5)	1	71.72	58.06	Endothermic	562	45.87
p-$HOC_6H_4HgL^1$	463-613	47.3(50.1)	1	89.66	79.25	Endothermic	558	59.20
p-$AcOC_6H_4HgL^1$	453-623	50.0(48.2)	1	42.17	28.88	Endothermic	553	73.33
$C_6H_5HgL^2$	453-523	47.3(46.3)	1	42.46	29.59	Endothermic	495	108.29
p-$HOC_6H_4HgL^2$	453-573	50.0(48.4)	1	50.99	38.99	Endothermic	518	128.92
p-$AcOC_6H_4HgL^2$	453-553	50.0(52.9)	1	20.14	4.93	Endothermic	501	55.25

EXPERIMENTAL

TG curves were recorded upto 1273K in air at a heating rate of 8° $\min^{-1}$ on G-70 thermo analyser, Setaram (Lyon, France). DSC curves were recorded upto 673K in air at a heating rate of 8° $\min^{-1}$ on DU Pont device.

C_6H_5HgCl [5], p-HOC_6H_4HgCl [6] and p-$AcOC_6H_4HgCl$ [7] were prepared by standard methods.

A solution of RHgCl (0.01 mol) in 25 ml 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 THF. The contents were stirred for about 3 h at room temperature and filtered. The filtrate was evaporated under vacuum to one-fourth of its original volume and petroleum ether was added. The $RHgL^1$ or $RHgL^2$ complexes separated out. These were filtered, dried and recrystallised from acetone.

From TG curves the weight loss accompanying the thermal degradation of the complexes has been calculated. In each case, the theoretical as well as calculated mass change corresponds to the formation of mercury(II) oxide. Beyond *ca*. 773K, HgO slowly volatilizes, leaving the crucible of the thermobalance empty. The DSC profile, in each case, shows an endothermic thermal effect corresponding to the decomposition of the complex to HgO. Thermal data are presented in Table 1.

RESULTS AND DISCUSSION

From 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 [8].

The order of reaction in each case is one. A comparison of the activation energy data for each set of complexes reveals that the p-acetoxyphenylmercuric derivative has the lowest value of E_a. This may be explained by the electron withdrawing effect of the acetoxy group, which leads to a weakening of R-Hg bond, thus making thermal degradation relatively easier. In case of p-hydroxyphenylmercuric analogue, the phenolic group is electron donating and the R-Hg bond is strengthened. Therefore, the activation energy value in this case is higher than in the unsubstituted phenylmercuric complex. This trend is observed in both the Kojic acid as well as the maltol series of complexes.

The Kojic acid complexes have higher activation energies and hence higher thermal stabilities as compared with the corresponding maltol derivatives. This may be attributed to steric reasons. In maltol complexes, the phenolic oxygen which is bound to the metal ion, is subject to steric repulsion due to the presence of a methyl group at C-2. This makes the thermal degradation relatively more spontaneous.

The apparent activation entropy ($\Delta S^{\neq}$) has been calculated by the method of Zsako' [9]. It has a positive value for all the complexes. Within a given series the p-hydroxyphenylmercuric complex has the highest value of $\Delta S^{\neq}$, while the p-acetoxyphenylmercuric analogue has the lowest. Thus, the former decomposes with the greatest degree of randomness while the latter with the least. For a particular R group, the Kojic acid complex has a higher value of $\Delta S^{\neq}$ than the maltol analogue.

The TG data are supplemented by DSC studies. Each complex shows an endothermic thermal effect corresponding to its decomposition to HgO. The heat of reaction ($\triangle H$) has been enumerated from DSC curves.

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