STUDIES ON THE THERMAL BEHAVIOUR OF TRIS-[THALLIUM(III)]-LACTATE

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ABSTRACT

The interaction of $Tl(OH)_3$ with excess lactic acid indicated the formation of $Tl(LA)_3$ where LA stands for the anion of lactic acid. The structure of the complex was predicted from elemental analyses and IR spectra. The thermal decomposition of the complex using TG, DTG and DTA gave supporting evidence for the predicted structure. The kinetics of thermal decomposition were also studied employing various computational methods.

INTRODUCTION

Currently, much work is being done on the thermal decomposition of metal carboxylates, particularly those of transition metals, to understand the mechanisms of decomposition and the nature of the decomposition products [1,2]. Recently, the thermal decomposition of metal chelates of salicylic acids were studied [3–7]. However, the thermal decomposition of carboxylates of heavy metals has received little attention. The present study deals with the TG, DTG and DTA of the Tl(III) complex with lactic acid. A search of the available literature showed that such a study has not been attempted so far. The Tl(III)–lactate bonding is discussed on the basis of IR spectra of the ligand and those of the complex. Various kinetic parameters, such as energy (E^*), enthalpy (H^*) and entropy (S^*) of activation, have been estimated by employing various computational methods, viz. Freeman–Carroll [8], Coats–Redfern [9], Horowitz–Metzger [10], and Fuoss methods [11].

MATERIAL AND METHODS

Preparation of Tl(III)-lactate

All the reagents used were of BDH AnalaR grade. Tl(III)-lactate was prepared by the method of Khadikar and Saxena [12]. Freshly precipitated

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Tl(OH)$_3$ was added to 1.0 M lactic acid solution until no more dissolved. The solution was digested on a water bath for 3–4 h, when the complex started to separate. The contents were cooled, filtered and washed with an ethanol–ether mixture (1 : 1 v/v), and dried in vacuum.

Elemental analysis

The composition of the complex Tl(LA)$_3$, where LA stands for the anion of lactic acid, was established by analysing Tl(III) iodometrically [13] and by the elemental analysis of carbon and hydrogen. Carbon and hydrogen were found to be 22.78 and 3.25%, respectively (calc: C, 22.9; H, 3.18%). No conductivity or NMR spectrum of the complex were measured because of its low solubility in the usual solvents.

IR spectra

The IR spectrum of the ligand and the complex was recorded on a Pye Unicam SP 1100 recording IR spectrophotometer. The samples were analysed as KBr discs. The exact position of each peak was checked by expansion of the peaks.
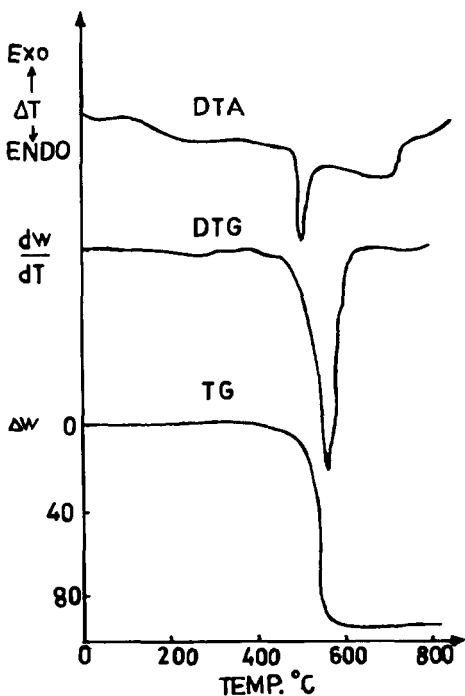

Fig. 1. DTA, DTG and TG curves of tris-[thallium(III)]-lactate.

Thermal analyses

Thermogravimetry (TG) of the sample (100.0 mg) was carried out on a Stanton-Redcroft recording thermobalance (HT-model) of 1-mg sensitivity in static air with a heating rate of 4°C min^{-1}. The chart speed was maintained at 3 in. h^{-1}. The sample was homogenised by sieving below 100 mesh and was packed as uniformly as possible in a platinum crucible of appropriate size.

A differential thermal analysis (DTA) assembly with F and M scientific 240 Hewlett-Packard temperature programmer, and a Platinet-II thermocouple (Engelhard, U.S.A.) were used. The DTA curve of the sample (40.0 mg) was recorded on a Rikadenki Kogyo recorder in static air at a heating rate of 4°C min^{-1}. Alumina was used as a standard reference material.

The TG, DTG and DTA results are shown in Fig. 1.

RESULTS AND DISCUSSION

Structure of the complex

The complex is thermally stable at room temperature, insensitive to air, thus, making the handling and kinetic measurements very easy. The IR spectrum of lactic acid shows a peak at 1695 cm^{-1} which is indicative of free carboxyl groups [14]. Upon coordination of lactic acid to Tl(III), a shift in this peak to a lower frequency (1675 cm^{-1}) was observed. This band was interpreted by Bush and Bailar [15] and by Kirschner [16] as being due to coordinated carboxylate groups. It was, thus, concluded that the carboxylate group of lactic acid is coordinated to the Tl(III) ion.

Comparing the C–O stretching frequencies of the secondary alcohol group of lactic acid with that of Tl(III)-lactate, it is found that the latter showed one strong band at 1350 cm^{-1}. This is to be expected because the coordination of the oxygen atom of the hydroxyl group to the metal ion will reduce its C–O stetching frequency. It may also be noted that the O–H bending peak at 1390 cm^{-1} remained almost in the same position for both lactic acid and its Tl(III) complex. This shows that there is no loss of proton by the alcoholic OH group upon coordination.

By analogy with Co(II)-lactate [17], the following structure is expected for the lactato complex of Tl(III).
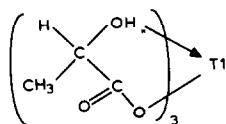
Thermal decomposition

An examination of the TG curve (Fig. 1) of Tl(III)-lactate indicates that the complex is stable up to 553 K, and beyond this temperature decomposes without the formation of any stable, isolable intermediate. The decomposition is completed at 848 K. The system covers the temperature range 553–923 K with a reaction interval of 823 K.

The DTA curve (Fig. 1) of the complex shows a broad endothermic band centred at 573 K. The corresponding weight loss at this temperature indicated the loss of three lactate moieties. The weight loss calculated from the TG curve is 55.15% (calc: 56.64%).

It is worth noting that Tl(III)-lactate decomposes through the formation of $Tl_2(CO_3)_3$. However, the final weight loss does not correspond to any of the possible end products, e.g., the formation of $Tl_2O_3/Tl_2O/Tl/2Tl_2O_3 \cdot Tl_2O$. This is in accordance with the observation made by Duval [18]. Accordingly, the disagreement of the final weight loss is due to the abnormal behaviour of the thallium metal, i.e., it undergoes volatilization followed by sublimation in the neighbourhood of 900 K.

Kinetic parameters

The data needed for the estimation of kinetic parameters employing different computational methods are given in Table 1 and discussed below.

The order of reaction, n, was determined by applying the Horo-witz–Metzger equation [10]: $C_s = n^{1/1-n}$, where C_s is the weight fraction of the substance present at the peak temperature, T_s (DTG peak temperature). The order of decomposition was calculated to be one. The order of reaction (n) was also determined graphically using the Freeman–Carroll method [8] and was found to be one. This method has also been used for the graphical calculation of the activation energy, E^*. Accordingly, a plot of $\Delta \ln(d\alpha/dT)/\Delta \ln(1 - \alpha)$ against $\Delta(1/T)/\Delta \ln(1 - \alpha)$ should yield a straight line, the slope of which gives E^*/R and the intercept at the Y-axis gives the value of n (Fig. 2). The activation energy (E^*) thus calculated is recorded in Table 2.

The Coats–Redfern equation [9] was also employed in the following form (suitable when $n = 1$, as in the present case) to calculate the activation energy (E^*)

$$\log \frac{\log C^{-1}}{T^2} = \log \frac{ZR}{\phi E^*} - \frac{E^*}{2.303RT}$$

where $C = (W_{0c} - W)/W_{0c}$; W_{0c} = total mass loss for the particular stage; W = mass loss at temperature T (K); Z = pre-exponential factor; R = gas constant; and ϕ = heating rate (°C s^{-1}). Plotting $\log(\log C^{-1}/T^2)$ against T^{-1}, a linear plot was obtained (Fig. 3). The activation energy obtained from

TABLE 1

Data required for the estimation of kinetic parameters for the thermal decomposition of tris-[thallium(III)]-lactate by different computational methods

Temp. (K)	$1/T \times 10^3$	Freeman–Carroll method		Coats–Redfern method		Horowitz–Metzger method	
		$\Delta \ln(d\alpha/dT)/\Delta \ln(1-\alpha)$	$\Delta 1/T/\Delta \ln(1-\alpha)$	$\alpha \times 10^3$	$\ln(\ln C^{-1}/T^2)$	θ	$\ln[\ln(W_0/W)]$
733	1.364	–	–	7.12	7.876	–80	–4.942
753	1.328	–3.445	12.354	36.12	7.188	–60	–3.399
773	1.294	–19.448	2.810	109.46	6.712	–40	–2.155
793	1.261	–12.000	1.000	218.93	6.406	–20	–1.342
813	1.230	–5.500	0.516	419.81	6.084	0	–0.608
832	1.200	–1.006	0.252	944.17	5.381	20	1.059
853	1.172	0.599	0.029	989.05	5.207	40	1.507

TABLE 2

Kinetic parameters for the thermal decarboxylation of Tl(III)-lactate

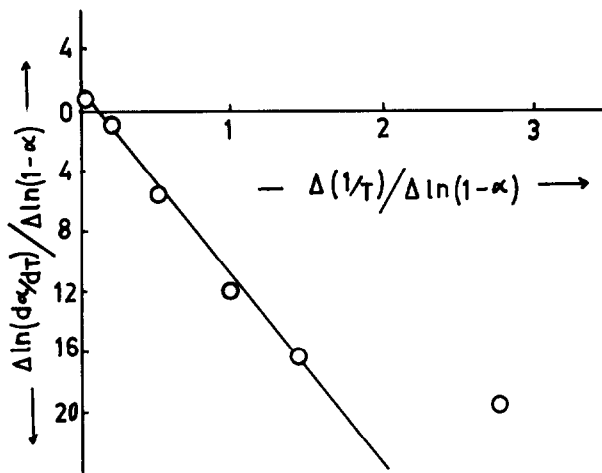| Method	T_i (K)	E^* (kcal mol^{-1})	H^* (kcal mol^{-1})	S^* (e.u.)	G^* (kcal mol^{-1})	$Z \times 10^{-14}$	$K_r \times 10^3$ (s^{-1})
Freeman–Carroll	813	63.16	61.54	–	–	–	–
Coats–Redfern	813	63.06	61.42	–3.250	65.702	2.930	3.528
Horowitz–Metzger	813	63.04	61.42	–3.232	65.667	2.318	2.680
Fuoss	813	63.36	61.73	–3.140	65.914	3.202	4.822

Fig. 2. Freeman and Carroll treatment for the decomposition of tris-[thallium(III)]-lactate.

the linear plot is recorded in Table 2. The method has also been used for the calculation of the pre-exponential factor (Z).

In addition to the above, the Horowitz–Metzger [10] and Fuoss [11] methods have also been used for the estimation of E^* and Z. In the former case, a plot of $\ln[\ln(W_0/W)]$ against θ gives a straight line (Fig. 4) with a slope of E^*/RT_s^2 (W_0 = initial weight; W = weight remaining at a given temperature; $\theta = T - T_s$; and T_s = reference temperature at which dW/dT is a maximum. The value of E^* thus obtained is presented in Table 2.

In the Fuoss method [11] the following equations, applicable to first-order
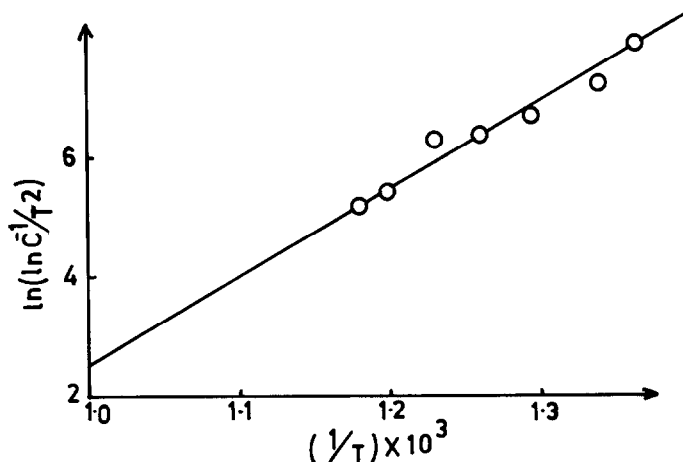

Fig. 3. Coats and Redfern treatment for the decomposition of tris-[thallium(III)]-lactate.
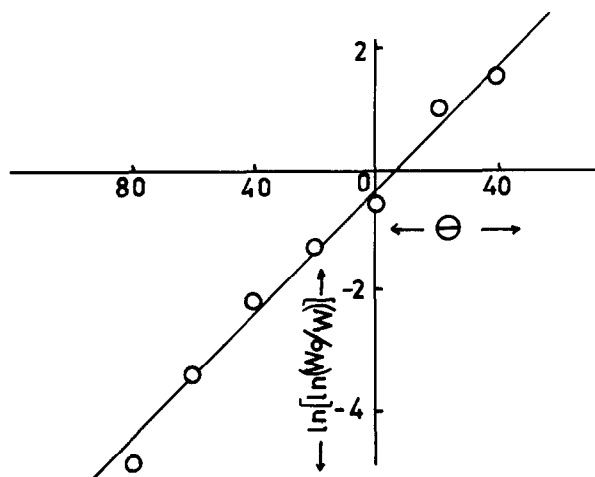
Fig. 4. Horowitz and Metzger treatment for the decomposition of tris[thallium(III)]-lactate.

kinetics, are used for the estimation of E^* and Z, respectively.

$$E^* = \frac{RT_i}{W_i}\left(\frac{dW}{dT}\right)_i$$

$$Z \equiv \frac{a}{W_i}\left(\frac{dW}{dT}\right)_i \exp(E/RT_i)$$

where W_i = weight at the point at which the TG curve changes from concave downwards to concave upwards, T_i = inflection temperature (K) at which dW/dT is a maximum (DTG peak temperature), and a is the heating rate. The estimated values of E^* and Z are also recorded in Table 2.

Using the inter-relationship [19] of Z with the activation entropy, S^*, the latter is estimated using the expression

$$S^* = (\log Zh/KT_i)R$$

where K is the Boltzmann constant and h the Planck constant.

As the reaction rate mainly depends on the free energy of activation, G^*, the activation entropy should decide the magnitude of G^* according to the equation

$$G^* = E^* - T_i S^*$$

From the rate-dependent parameters obtained above, the specific rate constant, K_r, is calculated from the relationship

$$K_r = Z \exp(-E^*/RT_i)$$

A perusal of Table 1 shows that the activation energy, E^*, for the decarboxylation lies around 63.00 kcal mol^{-1}, with an estimated uncertainty of ± 0.5 kcal mol^{-1}. These values are comparable with the generally accepted values of the activation energy of the decarboxylation reaction [1,2].

It is interesting to note that the activation energies obtained from different methods are close to each other. Such a good agreement could only be attributed to coincidence, because there are several steps involved in obtaining the final results, and each step could give rise to some error, for instance, error in curve-fitting and error in slope measurement. Unless some errors happen to cancel each other by chance, it would be impossible to obtain such a good agreement.

The activation enthalpy, H^*, has been evaluated from the relationship

$$H^* = E^* - RT_1$$

The values of E^* and H^* differ by an average of 1.00 kcal mol^{-1}. This small difference could not be differentiated experimentally and we could safely say that E^* and H^* are equivalent. The error limit in the values of H^* is ± 0.5 kcal mol^{-1}.

The magnitude of the negative value of the activation entropy suggests appreciable thermal decarboxylation of Tl(III)-lactate. This is clearly borne out from the shape of the corresponding TG curve.

The values of all the kinetic parameters (Table 1) obtained are within the range usually observed for a first-order reaction [1,2,20]. Thus, it can be concluded that the thermal decarboxylation of Tl(III)-lactate is a first-order reaction.

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