J. Iran. Chem. Soc., Vol. 7, No. 4, December 2010, pp. 846-852.

JOURNAL OF THE
Iranian
Chemical Society

Thermokinetic Studies of Organotin(IV) Carboxylates Derived from *para*-Methoxyphenylethanoic Acid

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(Received 22 May 2009, Accepted 16 December 2009)

Thremogravimetric (TG) studies of a new series of organotin(IV) carboxylates of the general formula R_nSnL_{4-n} (where R = CH_3, C_2H_5, C_4H_9, C_6H_5, C_6H_{11} and C_8H_{17}, n = 2, 3 and L = *para*-methoxyphenylethanoate anion) have been carried out. Horowitz and Metzger method has been used to calculate thermokinetic parameters. It has been found that diorganotin dicarboxylates have larger activation energy than those of corresponding triorganotin carboxylates. Furthermore, the activation energy, Gibb's free energy, entropy and enthalpy of diorganotin compounds shows the following trend, $(CH_3)_2SnL_2 < (C_2H_5)_2SnL_2 < (C_4H_9)_2SnL_2 < (C_8H_{17})_2SnL_2$. This is attributed to steady increase in chain length of the alkyl groups. However, triorganotin compounds do not show such behavior.

Keywords: Thremogravimetry, Organotin(IV) carboxylates, Thermokinetic parameters, Activation energy

INTRODUCTION

Organotin compounds are well known because of their biological and non-biological applications [1-7]. In this regards there are numerous articles and reviews available in the literature [8-13]. Their applications and structural chemistry is well documented, however, the chemistry related to thermokinetic parameters is yet to be explored as no significant data is available on this subject [14,15]. The organotin compounds are being used as pesticides, fungicides, bactericides, antifouling agents, catalysts and stabilizers [16]. Their use in architecture, agriculture, medicines and aircrafts is also recognized [17]. Therefore, thermokinetic parameters are required to asses the functional stability of a given organotin compound for its particular use value. As for as the material science is concerned, the solid state kinetic data (resulting from external stimuli, such as thermal activation by thremogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC)) has become highly useful in formulation and characterization of materials and technological processes [18-20]. The thermal behavior and properties are reflected by the thermokinetic parameters evaluated on the basis of a well established TG and DSC scans recorded at a certain heating rate and atmospheres (under nitrogen or air flow) for the degradation processes of a compound [21]. So for this purpose efforts are being exercised in experimentations to develop a correlation between the conversion degree and time in term of physical and chemical phenomena as affected by sample properties and measurement conditions.

Consequently we have performed thermal analysis of a new series of organotin carboxylates [22]. Different physical constants like activation energy (E_a), order of reaction (n), pre-exponential factor (A), enthalpy ($H^‡$), entropy ($S^‡$) and Gibbs

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*Corresponding author. E-mail: drdanish62@gmail.com free energy ($G^{\ddagger}$) have been calculated by various literature methods [23,24].

EXPERIMENTAL

Chemicals

All the organotin precursors were purchased from Aldrich chemicals (USA). *Para*-methoxyphenylethanoic acid was obtained from Fluka (Switzerland). All these chemicals were of analytical grade and used without further purification. The solvents were dried and purified according to the methods given in the literature [25].

Synthesis

All these complexes were prepared according to the literature method [22], briefly discussed here. Triorganotin carboxylates were synthesized by refluxing (4-6 h) an appropriate triorganotin halide with the ligand acid (*para*-methoxyphenylethanoic acid) using triethylamin in chloroform. After cooling to room temperature the reaction mixture was filtered and boiled with anhydrous activated charcoal and then filtered through silica bed. Solvent was completely removed under reduced pressure. The crude mixture was recrystallized from appropriate solvent. Diorganotin dicarboxylates were synthesized by refluxing the desired organotin oxide with stoichiometric molar ratio of the ligand acid under argon; in toluene for 6 h. Water formed during the reaction was continuously removed by the use of Dean-Stark apparatus. The isolation, purification, and crystallization were carried out as explained above. All these compounds are fairly soluble in DMSO and $CHCl_3$. These complexes were confirmed by comparing melting points and infrared data with literature report [22].

$$R_3SnX + LH \xrightarrow[\text{Cholorform}]{\text{Base}} R_3SnL + \text{Salt}$$

Where,

LH **(I)**, R= $-CH_3$ **(II)**, n-C_4H_9 **(V)**, $-C_6H_5$ **(VII)**, $-C_6H_{11}$**(VIII)**

$$R_2SnO + 2LH \xrightarrow{\text{Toluene}} R_2SnL_2 + H_2O$$

Where,

R= $-CH_3$ **(III)**, $-C_2H_5$ **(IV)**, n-C_4H_9 **(VI)**, n-C_8H_{17} **(IX)**

Instrumentation

Melting points were measured using an electrothermal melting point apparatus MP-D Mitamura Riken Kogyo (Japan) while infra red spectra recorded as KBr discs on a Perkin Elmer 16FPC FT-IR. The non-isothermal kinetics of decomposition was carried out on SDT Q600 V2.8 instrument using N_2 atmosphere. About 2-4 mg of compound was taken in platinum crucible, which gave a proportional signal to the recorder and computer interface to plot the weight loss of the sample against temperature. Each sample was subjected to controlled heating rate of 20 °C min^{-1} in the temperature range from 50 to 1000 °C. IR of the residue indicated only the presence of tin oxide.

RESULTS AND DISCUSSION

The TG and DTG curves are presented in Figs. 1 and 2,

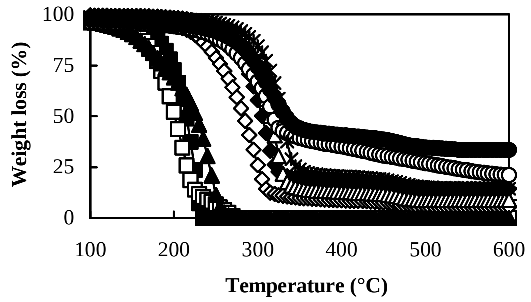

Fig. 1. TG curves for compounds I-IX: (■) I, (□) II, (◇) III, (◆) IV, (▲) V, (△) VI, (○) VII, (●) VIII, (✳) IX.

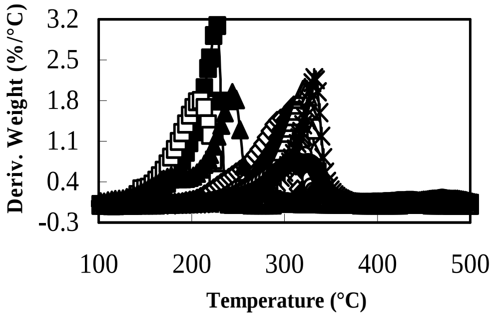

Fig. 2. DTG for compounds I-IX: (■) I, (□) II, (◇) III, (◆) IV, (▲) V, (△) VI, (◇) VII, (◆) VIII, (✳) IX.

respectively. The temperature value corresponding to the peak in DTG curve (Fig. 2) is known as T_s, the characteristic value where maximum degradation in a given step of the TG curve occurs and is further used to calculate the thermokinetic parameters [24]. Horowitz and Metzger plots with good values of R^2 are shown in Fig. 3. In order to have well defined peaks derivative of DTA has been presented (Fig. 4) for all the compounds. The experimental errors and standard deviations are not determined because kinetic parameters were calculated on a single thermal degradation scan. The thermokinetic parameters are given in Table 1 and 2. Except the ligand acid and tributyltin *para*-methoxyphenylethanoate, others show two step decomposition pattern. The activation energy for this series falls in between 9.59-140.52 kJ mol^{-1} while order of the decomposition covers 0.15-1.76 range. However, this order of reaction is different for both the steps. The decomposition pattern of each compound is discussed below individually, while the mass loss occurred is presented in the Table 3.

***Para*-methoxyphenylethanoic acid (I).** The ligand, *para*-methoxyphenylethanoic acid melts at 85 °C and shows single step decomposition in the temperature range 110-235 °C (Fig. 1), without leaving any residue. It is proposed that at the beginning stage CO_2 is evolved leaving behind *para*-methoxy toluene. This later on decomposes into methoxy and toluoyl radicals. This decomposition needs 113.77 kJ mol^{-1} of the activation energy and follows 0.18 order kinetics. Furthermore, Gibbs free energy and enthalpy for this process is 514.82 and 109.61 kJ mol^{-1}, respectively while entropy is -810 J Kmol^{-1}.

Trimethyltin *para*-methoxyphenylethanoate (II). This compound shows its melting point at 140 °C, indicated by an endotherm in derivative of DTA (Fig. 4a), and followed by a very sharp first step decomposition which is completed at 240 °C. This decomposition shows 90% mass loss due to detachments of the ligand (50% of total mass) alongwith 4/5 of Me_3Sn moiety. This step needs 81.57 kJ mol^{-1} of E_a and obeys 0.62 order kinetics. The remnant Me_3Sn, volatilizes in the second step (240-275 °C) with 33.85 kJ mol^{-1} activation energy and obeys 0.15 order of decomposition. The values of A, $S^‡$, $H^‡$ and $G^‡$ are given in the Tables 1-2.

Dimethyltin bis(*para*-methoxyphenylethanoate) (III). The thermal degradation trend of this compound (Fig. 1) is similar to that of compound (**II**) except the temperature ranges for the decomposition steps. It remains in the solid phase up to 66 °C (Fig. 4a) where melting occurs, after which it decomposes with bulk quantity upto 375 °C. The probable fragments detached during this decomposition are two moles of ligand (68.75%), alongwith loss of 0.6 mol of Me_2Sn (18.75%). For this mass loss activation energy and reaction order are 86.84 kJ mol^{-1} and 0.48, respectively. In the second step (375-515 °C), only 60% (0.24 mol) of the remaining mass of Me_2Sn, is volatilized giving ~5% residue of the initial mass taken for experimental run. The numerical data regarding thermokinetic parameters are given in Tables 1-2.

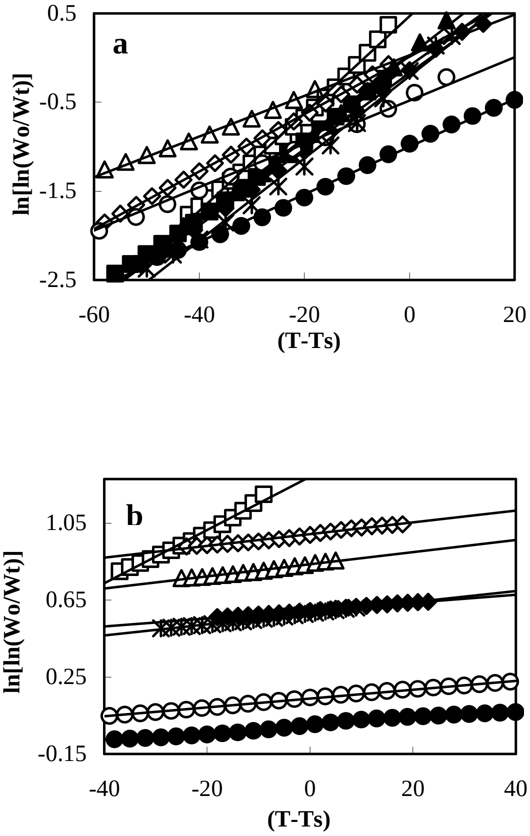

Fig. 3. Horowitz & Metzger plots (a) first step for compounds I-IX: (□) I, (■) II, (◇) III, (◆) IV, (△) V, (▲) VI, (○) VII, (●) VIII, (✳) IX and (b) second step for compounds II-IV and VI-IX: (□) II, (◇) III, (◆) IV, (△) VI, (○) VII, (●) VIII, (✳) IX.

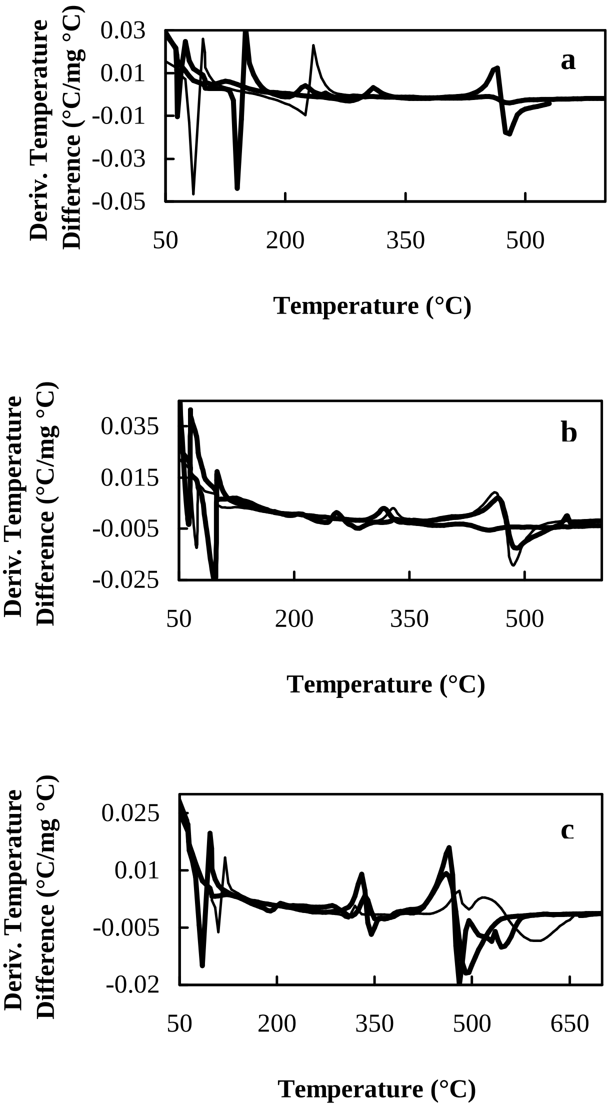

Fig. 4. Derivative of DTA for compounds (a) I-III: (–) I, (▬) II, (▬) III; (b) IV-VI: (–) VI, (▬) V, (▬) IV; and (c) VII-IX: (–) VII, (▬) VIII, (▬) IX.

Diethyltin bis(*para*-methoxyphenylethanoate) (IV). The thermal analysis of this compound describes its resistance towards physical or chemical transformation up to 90 °C, *i.e.*, its melting temperature, indicated by the endothermic peak in Fig. 4b. The weight loss with the rise of temperature shows two step degradation. The first step, 165-370 °C, can be interpreted by the partial release of ligand and diethyltin resulting in the 81% decrease in the total weight. In this step the requisite amount of activation energy is 121.50 kJ mol^{-1} showing half order kinetics. It appears from the exotherm at 463.74 °C (Fig. 4b) that oxygen from the ligand interacts with tin thus facilitating simultaneous removal of remaining ethyl groups as butane alongwith some quantity of Et_2Sn. For second step, 420-525 °C; the energy of activation is 9.59 kJ mol^{-1} and the reaction order is 1.65. About 15% residue in the form of tin oxide is left which contains 13% tin of starting material. The values of A, $S^{\ddagger}$, $H^{\ddagger}$ and $G^{\ddagger}$ are given in the Tables 1-2.

Tributyltin *para*-methoxyphenylethanoate (V). It starts to decompose after melting at 55 °C, indicated by an endotherm in the derivative of DTA graph (Fig. 4b). It follows single step decomposition, but the decomposition is relatively slower as compared to ligand acid and corresponding methyl derivative (Fig. 1). It is proposed that during the decomposition, first ligand is released followed by the complete volatilization of Bu_3Sn moiety upto 270 °C. A very small exotherm in (Fig. 4b) at 175-200 °C suggests that some sort of re-arrangement takes place which is resisted by steady increase in temperature and no pleatue/deflection is seen in the TG curve. For this degradation process the activation energy and order were 51.56 kJ mol^{-1} and 0.45, respectively (Table 1). The entropy value (-945 J Kmol^{-1}) for this compounds strongly documents its least stability in this series.

Dibutyltin bis(*para*-methoxyphenylethanoate) (VI). This compound melts at 70 °C; however, the TG curve (Fig. 1) shows that after melting it is stable up to 140 °C. It follows two steps thermal degradation, but the bulk percentage is eliminated in the first step (upto 400 °C). This step shows the 87% mass loss due to release of ligand and some Bu_2Sn. Hence its behavior is just like the compound-IV. For this step Ea is 136.81 kJ mol^{-1} and n is 0.49. In the second step (425-505 °C) degradation is also very similar to compound-IV. Oxygen from the ligand is interacting with tin associated with the release of butyl groups as butyl radical or octane alongwith some quantity of the Bu_2Sn as reflected from the derivative of DTA (Fig. 4b) and TG curves (Fig. 1). About four percent weight loss is associated with this step in the temperature range 340-470 °C. The Ea for this step is 14.85 kJ mol^{-1} and n is 0.33. Nine percent of the total mass of the complex is left as tin oxide in the form of residue, confirmed by infrared studies.

Table 1. Kinetics Parameters for the First Step of TG Curve

Comp.	T_s (°C)	R^2	Ea (kJ mol^{-1})	A (s^{-1})	n	$\Delta S^{\ddagger}$ (J K mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
I	227	0.9949	113.77	2.03×10^{11}	0.18	-810	109.61	514.82
II	209	0.9984	081.57	1.41×10^{08}	0.62	-871	077.56	497.48
III	296	0.9993	086.84	1.50×10^{07}	0.48	-888	082.11	587.22
IV	311	0.9989	121.50	1.57×10^{10}	0.50	-830	116.65	601.20
V	245	0.9956	051.56	1.78×10^{04}	0.45	-945	047.26	536.92
VI	323	0.9970	136.81	2.20×10^{11}	0.49	-808	131.86	613.59
VII	317	0.9953	070.66	2.14×10^{05}	0.28	-923	065.75	610.62
VIII	309	0.9973	075.39	7.71×10^{05}	1.76	-913	070.55	601.44
IX	333	0.9922	140.52	2.90×10^{11}	0.58	-806	135.48	623.83

Table 2. Kinetics Parameters for the Second Step of TG Curve

Comp.	T_s (°C)	R^2	Ea (kJ mol^{-1})	A (s^{-1})	n	$\Delta S^{\ddagger}$ (J K mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
II	270	0.9853	33.85	1.21×10^{02}	0.15	-099	29.33	564.94
III	466	0.9820	14.08	1.50×10^{-1}	1.52	-104	07.94	776.10
IV	468	0.9947	09.59	4.87×10^{-2}	1.65	-105	03.43	780.59
VI	474	0.9855	14.85	1.71×10^{-1}	0.33	-104	08.64	784.24
VII	440	0.9986	09.72	5.79×10^{-2}	0.61	-105	03.80	750.78
VIII	470	0.9767	08.26	3.35×10^{-2}	0.80	-105	02.09	783.63
IX	475	0.9916	13.50	1.24×10^{-1}	1.18	-104	07.28	785.89

Table 3. Mass Loss (%) in the First and Second Steps of TG Curve

Comp·	Mass loss (%) in the first step		Mass loss (%) in the second step	
	Observed	Calculated	Observed	Calculated
I	100	100	-	-
II	90.7	90.0	09.3	10.0
III	88.6	87.5	05.9	07.5
IV	81.3	82.5	03.4	03.5
V	100	100	-	-
VI	87.2	87.0	04.0	04.1
VII	63.4	64.5	16.0	15.5
VIII	60.7	62.0	05.9	04.6
IX	79.2	78.0	06.2	07.0

Triphenyltin *para*-methoxyphenylethanoate (VII). An endotherm at 110 °C in the derivative of DTA curve (Fig. 4c) for this compound matches with its melting temperature. The TG curve shows two step mass loss pattern. In the first step (150-380 °C), 1 mole of the ligand and 2.17 mol of phenyl groups are evolved, corresponding to the 64.5% weight loss. This is relatively faster step as compared to the second one with T_s at 317 °C (Fig. 2) and needs 70.66 kJ mol^{-1} E_a and obeys 0.28 order kinetics of decomposition. This step is completed at 380 °C, leaving behind C_6H_5Sn which seems to be more stable than the original complex as revealed by the analysis of thermodynamic state functions. It slowly decomposes over a very long range of temperature (380-650 °C). In this step 3% of Sn is also lost as a volatile material alongwith remaining phenyl group. This step has a bit higher value of reaction order (0.61) but relatively low value of activation energy (9.72 kJ mol^{-1}) as compared to previous step. The material left as residue that contains 19.8% tin of the starting compound.

Tricyclohexyltin *para*-methoxyphenylethanoate (VIII). This compound showed thermal behavior similar to compound (**VII**). It is a semisolid compound which shows physical transformation towards the fluid phase between 50-185 °C. This is followed by a sharp decomposition between 200-410 °C (62% weight loss), attributed to the departure of one mole of ligand and ⅔ of the cyclohexyl groups. This step requires 75.39 kJ mol^{-1} activation energy of thermolysis obeying 1.76 order mechanism. The second step (410-540 °C) is very slow cleavage of 29.6% of the remaining cyclohexyl group of the compound. The derivative of DTA (Fig. 4c) shows a sharp exotherm in this region which is due to interaction of tin with oxygen. This step follows 0.80 order of reaction and needs 8.26 kJ mol^{-1} of activation energy. The residue found is ⅓ of the original mass.

Dioctyltin bis(*para*-methoxyphenylethanoate) (IX). This compound showed stability up to 180 °C after its fusion at 85 °C. In the first step there is release of two moles of ligand and ¾ mol of octyl groups, alongwith about 5% loss of tin as volatile material. This step involves the largest energy of activation in this series (140.50 kJ mol^{-1}), probably due to intra- or inter-molecular entanglement of the octyl groups. This step prolonged to 390 °C with total weight loss of 79%. The remnant of the alkyl group escapes in the second step which occurs in the range of 425-530 °C leaving tin oxide (14.5%) as the residual component.

CONCLUSIONS

The activation energy follows an interesting trend in this series. Diorganotin dicarboxylates *e.g.* methyl and butyl have larger activation energy than those of corresponding triorganotin carboxylates. This is due to the cumulative effect of four oxygen atoms simultaneously bonded to tin in these compounds which enhance their thermal stability. For diorganotin dicarboxylates the activation energy decreases with a decrease in the chain length of the R-group. In this regards largest activation energy is shown by dioctyl derivative. It is proposed that a long chain bulky group may wrap the tin moiety or entangles with tin as well as rest part of the molecule thus providing more hindrance to thermal decomposition. It is suggested that organotin carboxylates of longer chain R-groups are thermally more stable. A very similar trend of Gibb’s free energy is observed for diorganotin dicarboxylates.

Triorganotin carboxylates, however, do not obey such regular fashion, rather a slightly reverse order is observed. These are thermally less stable than corresponding diorganotin dicarboxylates. The reduction in their thermal stability is attributed to reduction in number of oxygen atoms bonded to tin. Among triorganotin carboxylates, trimethyl derivative shows more stability which is due to its more electronegative nature that provides comparatively more strength to the Sn-C bond than those of other groups. Contrary to diorganotin dicarboxylates, Gibb’s free energy for triorganotin carboxylates does not show a regular trend.

The diorganotin complexes show more disorder as reflected by the higher values of their entropy (Table 1-2) than those of triorganotins. The dioctyl derivative (compound VIII) shows the highest entropy value as it may act as wrapping material for this compound. The entropy value steadily decreases as we move from octyl to methyl through butyl and ethyl groups. Similar to activation energy and Gibb’s free energy, triorganotin carboxylates do not show a regular trend for entropy. Further investigations to resolve this issue are under process.

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