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Kinetic Studies of the Thermal Decomposition of di- and tri-Organotin Derivatives of 1-Nitroso-2-Naphthol

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The di- and tri-organotin complexes of general formula R_2SnL_2 and R_3SnL where R = C_4H_9, C_6H_5, $C_6H_5CH_2$, C_6H_{11} and L=1-nitroso-2-naphthol, were subjected to thermal decomposition by means of thermogravimetry (TG). The decomposition occurred in steps and the kinetics of every set of reactions were determined using the method described by Coats and Redfern. These results were analysed to establish the decomposition kinetics and hence to calculate activation energies. The activation energies were also determined by applying the method described by Horowitz, which yielded comparable results.

Introduction

Thermal analysis, although an old technique, is now proving useful in the interpretation and determination of different physical parameters such as inorganic and organic thermodynamics and reaction kinetics in different fields of study such as chemistry, polymer science, biology, medicine and pharmaceutics[1–8].

In view of our previous work in synthesis, characterization and biological studies of main group complexes specially organotin[9–21], we are interested in thermal studies of organotin compounds. In this paper we report the thermal decomposition, activation energies and order of reactions of organotin complexes of 1-nitroso-2-naphthol.

Experimental

The synthesis and characterization of organotin complexes of 1-nitroso-2-naphthol have been reported previously[9,20]. The TG curves were recorded on a Netzsch simultaneous thermal analyzer STA 429. The samples were contained in an alumina crucible A1203 which was then adjusted on a palladium-ruthenium crucible support platform, which gave a proportional signal to the recorder and computer interface to plot the weight loss of the sample against temperature. The heating rate was 10 deg/min. All experiments were performed under aerobic conditions.

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Results and Discussion

The thermal decomposition of the complexes was studied to investigate their thermal stability, purity and fragmentation pattern in the temperature range $20 - 1200^{\circ}$C. The thermal behaviour of the investigated compound in terms of intermediate and volatiles, based on the coincidence between the calculated and the found values are given in Table 1. The reaction order was calculated according to the method described by Coats[22].

Table 1. Thermal behaviour of the investigated compounds

No. Compound*	Temp. range (°C)	Wt. Found	Loss % Calc.	Volatile evolved	Corresponding intermediate
1. $(C_4H_9)_3SnL$	200-350	31.72	30.73	$C_{10}H_6O$	$C_{12}H_{27}NOSn$
2.	360-550	24.89	24.68	$2C_4H_9$	C_4H_9NOSn
3. $(C_6H_5)_3SnL$	160-420	22.69	23.95	$C_{10}H_5$	$C_{18}H_{16}NO_2Sn$
4.	430-680	13.13	14.75	C_6H_5	$C_{12}H_{11}NO_2Sn$
5.	690-740	8.58	9.00	HONO	$C_{12}H_{10}Sn$
6. $(C_6H_{11})_3SnL$	130-660	31.60	30.74	$2C_6H_{11}$	$C_{16}H_{17}NO_2Sn$
7.	690-800	6.19	5.55	NO	$C_{16}H_{17}OSn$
8. $(C_6H_5CH_2)_3SnL$	150-510	46.74	46.63	$C_{10}H_6NO_2+C_7H_7$	$C_{14}H_{14}Sn$
9.	560-1000	14.07	13.65	C_6H_5	C_8H_9Sn
10.$(C_6H_5CH_2)_2SnL_2$	220-440	33.85	33.64	$C_{10}H_6+C_7H_7$	$C_{17}H_{13}N_2O_4Sn$
11.	460-730	9.57	10.23	C_4H_2O	$C_{13}H_{11}N_2O_3Sn$
12.	750-810	5.25	4.65	NO	$C_{13}H_{11}NO_2Sn$
13.	840-940	10.9	11.78	C_6H_4	$C_7H_7NO_2Sn$

* L=1-nitroso-2-naphthol.

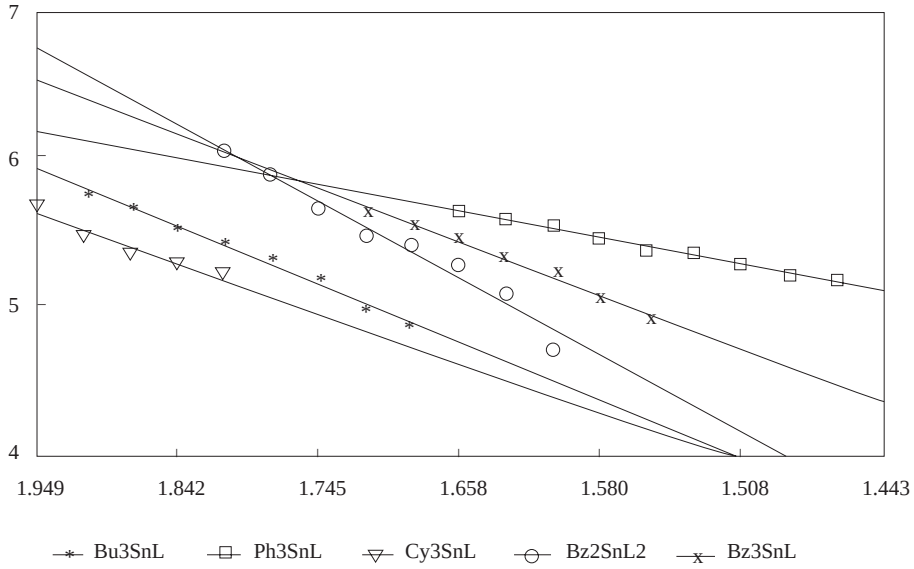

Figure 1. Decomposition Kinetics of Organotin Complexes using Coats' method for 1st step.
$1/T\cdot10^3$ (X-Axis) Vs $-\log[1-(1-\alpha)^{1-n}]/[T^2(1-n)]$ for $n \neq 1$ and $-\log[-\log(1-\alpha)]/(T^2)$ for $n = 1$ (Y-Axis).

Table 2. Values of activation energy of thermal decomposition of investigated compounds.

No.	Range of α studied	Standard deviation	Order n	Activation energy, (E Kcal/mol) Coats' method	Horowitz's method
1.	0.33-0.91	0.0183	1.5	18.034	14.68
2.	0.74-0.99	0.0040	1	21.19	24.93
3.	0.45-0.75	0.0049	2	10.93	14.17
4.	0.80-0.99	0.0018	1.25	11.91	9.70
5.	0.82-0.98	0.0016	1.1	34.78	32.90
6.	0.34-0.73	0.0104	1.5	14.13	13.18
7.	0.83-0.97	0.0013	1.5	22.00	21.98
8.	0.51-0.96	0.0124	1.25	20.37	18.90
9.	0.91-0.99	0.0005	1	9.68	13.88
10.	0.22-0.95	0.0275	1.5	26.77	22.20
11.	0.92-0.99	0.0004	1.25	15.44	12.69
12.	0.89-0.98	0.0004	1.20	29.73	25.97
13	0.87-0.99	0.0010	1.1	31.36	32.08

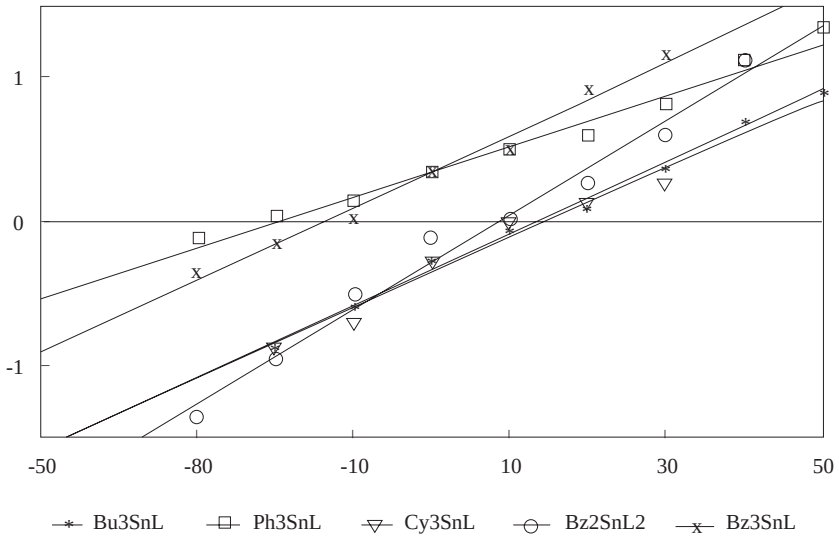

Figure 2. Decomposition Kinetics of Organotin Complexes using Horowitz's method for 1st step. θ (X-Axis) Vs $\ln\ln[(W_0 - W_f)/(W_t - W_f)]$ (Y-Axis).

TG data were used to calculate the relationship between

$$-\log[1-(1-\alpha)^{1-n}]/[T^2(1-n)] \quad \text{and} \quad 1/T.10^3 \quad \text{for} \quad n \neq 1$$

and

$$-\log[-\log(1-\alpha)]/(T^2) \quad \text{and} \quad 1/T.10^3 \quad \text{for} \quad n = 1.$$

The reaction order determined in this way is given in Table 2. Similarly, activation energy values calculated using both methods[22,23] are given in Table 2 and are in reasonable agreement. Figures 1 and 2 show the representative use of thermogravimetric data using the methods described by Coats and Horowitz respectively.

The thermal decomposition pattern of R_3SnL and R_2SnL_2 where R = C_4H_9. C_6H_5, $C_6H_5CH_2$, C_6H_{11} and L=1-nitroso-2-naphthol shows a different decomposition pattern due to the different R groups attached to the organotin moiety. For Bu_3SnL, two step decomposition was observed. In the first step a 31.72% loss in weight due to the loss of $C_{10}H_6O$ whereas in 2nd step a 24.89% loss in weight due to two C_4H_9 groups were observed in the temperature range $200-350^\circ$C and $360-550^\circ$C respectively. The first step was of order 1.5 with activation energy of 18.03 Kcal/mole and the 2nd step was of order 1 with activation energy 21.19 Kcal/mole.

Ph_3SnL followed a three step decomposition pattern. The first step showed a 22.69% weight loss at temperature range $160-420^\circ$C due to loss of $C_{10}H_5$ with order 2 and activation energy 10.93 Kcal/mole. In the 2nd step a 14.94% loss in weight was due to one C_6H_5 group with order 1.25 and activation energy 11.91 Kcal/mole at temperature range $430-680^\circ$C. In the third step at temperature range $690-740^\circ$C, OH and NO molecules were evolved with a 9.20% loss in weight. This decomposition was of order 1.1 with activation energy of 34.78 Kcal/mole.

Cy_3SnL exhibited a two step decomposition process. The first step showed loss of two C_6H_{11} groups with a 31.60% weight loss ($130-660^\circ$C). This step required an activation energy of 13.17 Kcal/mole with order 1.5. In the 2nd step ($690-800^\circ$C), a NO molecule was evolved with a 6.19% loss in weight and the overall reaction was of order 1.5, with an activation energy of 22.00 Kcal/mole.

Bz_3SnL again involved two types of decomposition. In the first step one molecule of ligand and one of the C_7H_7 group were eliminated in the temperature range $150-510^\circ$C with a 46.74% weight loss. This step was of order 1.25 and required an activation energy of 20.31 Kcal/mole. In 2nd step ($560-1000^\circ$C) one C_6H_5 group was evolved involving a 13.83% weight loss. This step was of order 1 and required 9.68 Kcal/mole activation energy.

Bz_2SnL_2 underwent four step decomposition. In the first step, a loss in weight of 33.85% was observed in the temperature range $220-444^\circ$C, indicating the loss of $C_{10}H_6$ and one C_7H_7 group from the system. This reaction was of order 1.5 with 26.77 Kcal/mole activation energy. In the 2nd step, a weight loss of 9.57% with order 1.25 and 15.44 Kcal/mole activation energy involved the elimination of C_4H_2O from the system in temperature range $460-730^\circ$C. In 3rd step ($750-810^\circ$C) and 4th step ($840-940^\circ$C) NO and C_6H_4 were evolved with weight losses of 5.25% and 10.9% respectively. The order and activation energies for 3rd and 4th steps were 1.20, 25.97 Kcal/mole and 1.1, 31.36 Kcal/mole respectively.

Conclusion

From the above discussion it can be concluded that in all the compounds except Bz_3SnL, either the ligand as a whole or part of the ligand evolved first. This proves the stability of Sn-C bond compared with Sn-O bond. Similarly, in most cases second step decomposition requires more energy compared with first step which is further evidence for Sn-C bond stability.

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