Organotin Complexes of Donor Ligands-Part-II-Intramolecular Coordination and Evaluation of Equilibrium Energy for 1-Nitroso-2-naphthoxy Tin Derivatives by Dynamic Infrared

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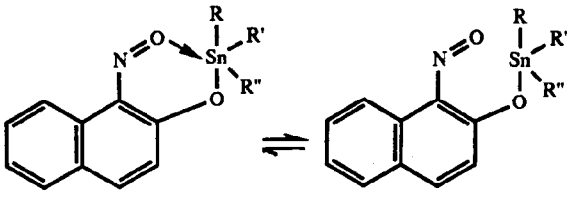
Summary: Dynamic infrared studies on 1-nitroso-2-naphthoxy organotin derivatives in temperature range 298-527 K have been carried out. Energy of equilibration, as calculated from Arrhenius equation, has been found between 2.15-4.849 KJ/K mole.

Introduction

Previously in Part-1 [1] we have reported synthesis of 1-nitroso-2-napthoxy triphenyltin (1), 1-nitroso-2-napthoxy tributyltin (2), 1-nitroso-2-napthoxy trichlorotin (3) and bis (1-nitroso-2-napthoxy) dichlorotin (4). These were characterized by different analytical techniques such as elemental analysis, infrared, electronic and NMR spectroscopy. Thermal analysis data and biological activity were also reported. In continuation of our previous work, dynamic infrared studies of the compounds have been made in certain range, i.e. 900 cm^{-1} , 750 cm^{-1} and 650 cm^{-1} 250 cm^{-1}. From this data energy of equilibration has been calculated as previously reported by different authors for analogous cases of silicon [2,3].

It is observed that organotin derivatives of 1-nitroso-2-naphthol in solid state have N=O⋯→Sn coordinate covalent bond at room temperature which is very sensitive for variable temperature infrared studies. It is proposed that before decomposition, reversible reaction takes place at certain range of temperature.

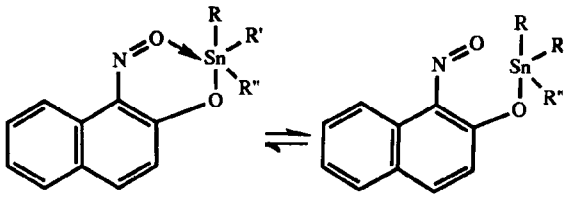


However the decomposition occurs at 523 K, after which no reversible equilibrium is observed. Recently similar intramolecular O⋯→Sn bonding is reported by Pan and co-workers [4].

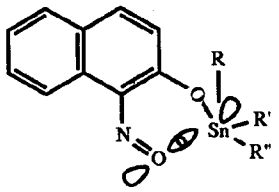
Results and Discussion

Infra red spectra of compound (1-4) do not differ much in the absorption of 1-nitoros-2-naphthoxy group. In free ligand $\nu_{N=O}$ stretching frequency appears at 852 cm^{-1} whereas in tin derivatives it appears at 837 cm^{-1}. The difference of 15 cm^{-1} is consistant with the presence of intramolecular N=O⋯→Sn coordinate bond, which in these molecules seems to be due to ease in building up a six membered ring required for the O⋯→Sn coordination. Measurement of $\nu_{N=O}$ for all compounds in solid state at temperature range 298 K - 523 K gave the following results.

When N=O group is coordinated with tin, a peak is observed at 837 cm^{-1}. At 323 K (50°C) the intensity of this peak decreases where a new peak appears in 860-875 cm^{-1} range which belongs to non-coordinated N=O group. By further heating at 348 K, 423 K and 473 K the intensity of new peak increases where peak at 837 cm^{-1} becomes shorter. If we reverse the temperature back to 298 K, the same pattern is reversed for the spectra. But after heating the sample to 523 K, reverse pattern is not observed which is evidence for the decomposition of the samples (Fig. 1 and 2). From the above observation the following equilibrium can be proposed between 298-473 K for which the energy of equilibration (E_{eq}) is calculated.



The formation of O-->Sn bond is interpreted in terms of hypervalence theory developed for the main group elements by Musher [5]. According to this theory three centered four electron (3c-4e) bond is formed between O - Sn - R as shown:



Interesting results were observed for Sn - O and Sn - Cl stretching vibrations in the range of 650-250 cm^{-1}. The intensities of both peaks decrease with increase in temperature and at certain temperature i.e. 523 K both the peaks disappear which is evidence for decomposition (Figs. 1 and 2).

Table 1: Different experimental conditions

Compound	Molar ratio	Solvent	Reflux/ Stir time	Compound ppted/ in solvent	m.p. (°C)
1-Nitroso-2-naphthoxy triphenyltin	1:1	$CHCl_3$	4 hr.(s)	in solvent	68-70
1-Nitroso-2-napthoxy trichlorotin	1:1	Petroleum ether	4 hr.(s)	ppted	185-188
Bis-(1-nitroso-2-napthoxy) dichlorotin	1:2	Petroleum ether	4 hr.(s)	ppted	165-168
1-Nitroso-2-napthoxy tributyltin	1:1	DMF	24 hr.(R)	in volvent	80-82

*Molar ratio order, tin salt: ligand.

Energy of equilibration (E_{eq})

We measured the absorbance A of N=O band for compounds (1-3) in temperature range 298-523 K (Table-2). By using Arrhenius equation, $\ln k = \ln A - E_{eq}/RT$ [6] and plotting graph between 1/lnk vs T (absolute temperature K), E_{eq} was calulated from slope as E_{eq} = R/slope where E_{eq} is the energy of equilibration (Table 3).

lnk was estimated from the relative optical densities of N=O group in bonded and non-bonded form of complex.

From the values of E_{eq} it can be safely said that in trichloro derivative (3) the O-->Sn bond is stronger than in tributyl derivative (2) which is stronger than triphenyl derivative (1). The strength of the bond can be explained in terms of electron withdrawing effect of chlorine, as a result of which $p\pi$ - $d\pi$ type of interaction becomes more favourable to form a stronger 3c-4e bond. In case of triphenyl derivative the steric hindrance of bulky phenyl groups (as well as naphthyl group) weakens the $p\pi$-$d\pi$ interaction, which results in a low value of E_{eq}.

Experimental

Reagent and apparatus

All the reagents used were of analytical grade and different analytical techniques were used for characterization as reported earlier [1]. For dynamic infrared studies in range 900 cm^{-1} - 750 cm^{-1} and 650-250 cm^{-1} in solid state as KBr discs, an infrared spectrophotometer with data processor Model 270-50 Hitachi, Japan and variable temperature accessory was used.

Table 2: Rate constant(k) from dynamic infrared for investigated compounds

Temp.	Compound-1			Compound-2			Compound-3		
	A_1	A_2	k=A2/A1	A_1	A_2	k=A2/A1	A_1	A_2	k=A2/A1
298	0.07	0.219	3.128	0.250	0.436	1.744	0.32	0.536	1.675
323	0.21	0.332	1.580	0.245	0.430	1.755	0.17	0.439	2.682
348	0.155	0.284	1.851	0.244	0.422	1.729	0.22	0.439	1.995
373	0.128	0.239	1.867	0.227	0.402	1.775	0.22	0.390	1.756
398	0.116	0.235	2.025	0.221	0.350	1.583	0.21	0.376	1.790
423	0.140	0.237	1.692	0.212	0.319	1.504	0.20	0.326	1.63
473	0.144	0.183	1.605	0.209	0.229	1.095	0.165	0.260	1.575
523	-	-	-	0.191	0.227	1.188	0.16	0.20	1.250
298	-	0.244	-	0.123	0.20	1.626	0.30	0.333	1.111

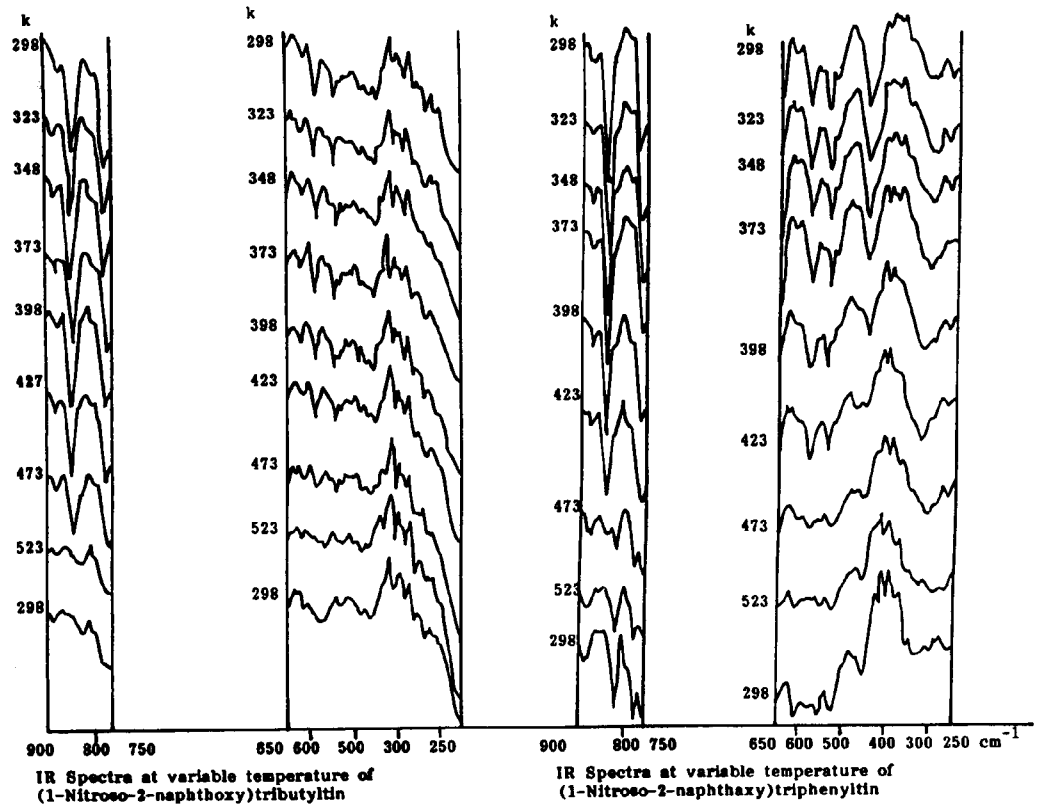


Fig. 1: Infrared spectra at variable temperature in 750 - 900 cm^{-1} and 20-650 cm^{-1} range for compound 1 and II.

Table 3: Energy of equilibration for investigated compounds

	Compound	E_{eq}(KJ K^{-1}mole^{-1})
(1)	$(C_6H_5)_3$ Sn L	2.150
(2)	$(C_4H_9{}^n)_3$ Sn L	4.157
(3)	Cl_3Sn L	4.849

General method for synthesis and dynamic infrared studies

General procedure for synthesis

All the compounds were prepared in dry organic solvents and inert atmosphere by stirring or refluxing 1:1 or 1:2 molar ratio of the precursors (details are given Table 1). The resulting compounds were either filtered or extracted from the solvents on removing the solvent by rotary evaporator. All the compounds were recrystallized and purified by thin-layer chromatography for further characterization.

Sample was mixed with KBr (1:100) and pellet was formed, which was used further for variable temperature infrared studies in temperature range 298-523 K.

Acknowledgement

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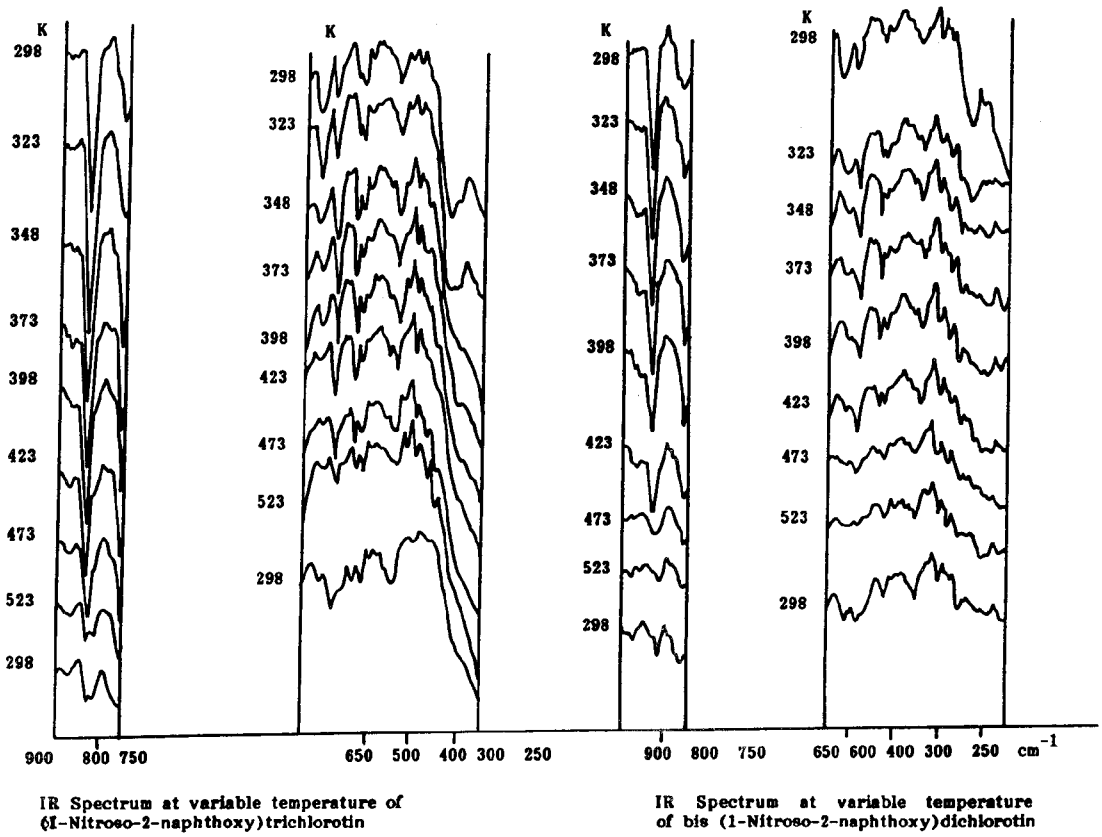

Fig. 2: Infrared spectra at variable temperature in 750-900 cm^{-1} and 250-650 cm^{-1} range for compound III and IV.

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