



Lewis Acid Nature of SnCl_4 and $n\text{-Bu}_2\text{SnCl}_2$ Determined by Adduct Formation with 3-Methyl-1-Indanone

MUHAMMAD DANISH^{1*}, C.M. ASHRAF², ALI MOHAMMAD³ AND FAIZ-UR-REHMAN³

^{1*}Department of Chemistry, University of Sargodha, Sargodha, Pakistan

²Department of Chemistry, F.C. College University, Lahore, Pakistan

³Department of Chemistry, University of the Punjab, Lahore, Pakistan

Abstract

Lewis acid nature of SnCl_4 and $n\text{-Bu}_2\text{SnCl}_2$ has been studied using 3-methyl-1-indanone. The equilibrium constant has been calculated for both the tin moieties. It has been found that Lewis acid character of SnCl_4 is fourteen times greater than that of $n\text{-Bu}_2\text{SnCl}_2$.

Key words: *Lewis Acid Nature, Adduct Formation, 3-Methyl-1-Indanone*

Introduction

Tin is inert and does not react with air or water at room temperature. However, at elevated temperatures, it forms a very thin oxide layer on the surface. Tin behaves in an amphoteric way and this nature depends upon concentration and temperature of the medium [1,2].

There are numerous reports on synthesis and applications of organotin compounds [3-8]; however, study of Lewis acid nature of tin halides and organotin halides covers the academic interest. In tin halides, organotin halides and most of organotin compounds, the tin center behaves as Lewis acid. Crystallographic data show, that tin center may show coordination number up to seven [10]. If a donor atom is much away from tin, it does not affect the coordination number and this state is also retained in non coordinating solvents [7,8,12].

Due to Lewis acid character of tin center, it can be used to study basic properties of compounds containing donor atoms. Compounds containing carbonyl group fit in this category as they act as Lewis bases.

In the present work, 3-methyl-1-indanone has been selected to study acidic properties of SnCl_4 and $n\text{-Bu}_2\text{SnCl}_2$. Furthermore, it is an important ligand in the synthesis of various tricarbonyl chromium complexes [13-15].

Experimental

All the chemicals were of analytical reagent grade (purchased from Merck) and used without further purification. Fresh distilled benzene was used whenever required.

Preparation of 3-methyl-1-indanone

Dry benzene (50 cm^3) [16] was taken in a two-necked round bottom flask equipped with a water condenser and magnetic stirrer. Crotonic acid (6.5 g) was then added followed by portionwise addition of anhydrous AlCl_3 (31.8 g), under inert atmosphere. The reaction being exothermic started without heating. Afterwards, the reaction mixture was refluxed for five hours. The reaction mixture was cooled, extracted in dry benzene, washed with distilled water to remove unreacted AlCl_3 . The organic layer was separated and treated with an aqueous solution of sodium

*Author for Correspondence

bicarbonate to remove un-reacted crotonic acid and β -phenyl butyric acid (by product). The organic layer was separated and washed twice with distilled water. The benzene extract was dried over $MgSO_4$ for several hours and filtered. Benzene was removed under reduced pressure. The residue was dissolved in dry ether (100 cm^3), stirred with activated charcoal for several hours and filtered through alumina. The filtrate was concentrated to half of its volume and kept overnight. The 3-Methyl-1-indanone was obtained as a crude mass, which was purified by distillation under reduced pressure [17].

Measurement of absorption and equilibrium constant

A stock solution of indanone ($3.8 \times 10^{-3}\text{ M}$) was prepared. Its molar concentration was kept constant throughout the experiment with both tin halides. The molar concentration of tin halides was varied for each determination. Stoichiometric

amounts of indanone and tin halide were mixed and absorption was measured at various wavelengths using UV-6000 UV-Vis-spectrophotometer, R&M Marketing, England. The absorbance was calculated using Beer-Lambert law.

Discussion

ortho-Dichlorobenzene was chosen as the solvent for studying the basicity of the ketone towards tin halides. Concentration of ketone was maintained constant while the concentration of $SnCl_4$ or $n\text{-Bu}_2SnCl_2$ was varied as far as experimentally possible.

The absorption data are given in Tables 1 and 2. The absorption spectra of neat of 3-methyl-1-indanone and with tin moieties are shown in Figs. 1 and 2. On adding $SnCl_4$ or $n\text{-Bu}_2SnCl_2$ (as solution in *ortho*-dichlorobenzene),

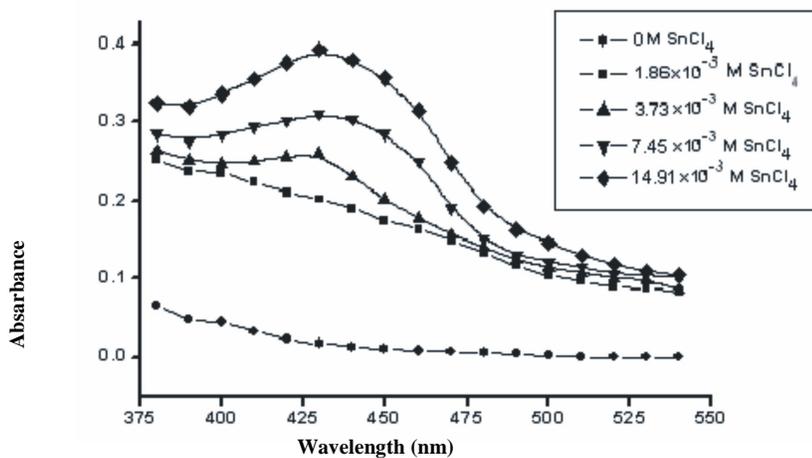
Table 1. Absorption data for 3-methyl-1-indanone* with $SnCl_4$.

S. No.	Wave Length (nm)	Concentration of $SnCl_4$ (M)				
		0	1.86×10^{-3}	3.73×10^{-3}	7.45×10^{-3}	14.91×10^{-3}
1	380	0.065	0.252	0.264	.285	0.325
2	390	0.048	0.237	0.252	0.276	0.320
3	400	0.044	0.235	0.247	0.284	0.336
4	410	0.032	0.223	0.250	0.293	0.354
5	420	0.022	0.210	0.256	0.302	0.376
6	430	0.017	0.202	0.260	0.310	0.392
7	440	0.013	0.190	0.230	0.304	0.380
8	450	0.010	0.174	0.202	0.285	0.356
9	460	0.008	0.163	0.177	0.250	0.315
10	470	0.007	0.149	0.156	0.190	0.248
11	480	0.006	0.133	0.140	0.150	0.192
12	490	0.004	0.116	0.124	0.130	0.162
13	500	0.002	0.103	0.114	0.122	0.146
14	510	0.000	0.096	0.107	0.114	0.130
15	520	0.000	0.089	0.101	0.106	0.118
16	530	0.000	0.087	0.098	0.104	0.109
17	540	0.000	0.084	0.086	0.102	0.104

* Concentration of 3-methyl-1-indanone taken each time is $3.84 \times 10^{-3}\text{ M}$

Table 2. Absorption data for 3-methyl-1-indanone* with $n\text{-Bu}_2\text{SnCl}_2$.

S No.	Wave Length (nm)	Concentration of $n\text{-Bu}_2\text{SnCl}_2$ (M)				
		0	1.8×10^{-2}	5.4×10^{-2}	10.8×10^{-2}	16.3×10^{-2}
1	380	0.078	0.085	0.100	0.103	0.108
2	390	0.054	0.060	0.071	0.075	0.084
3	400	0.041	0.050	0.060	0.064	0.068
4	410	0.025	0.029	0.039	0.043	0.048
5	420	0.011	0.020	0.026	0.029	0.032
6	430	0.005	0.014	0.020	0.022	0.028
7	440	0.001	0.010	0.016	0.018	0.023
8	450	0.000	0.008	0.012	0.014	0.021
9	460	0.000	0.005	0.011	0.013	0.018
10	470	0.000	0.004	0.009	0.011	0.016
11	480	0.000	0.003	0.007	0.009	0.014
12	490	0.000	0.002	0.006	0.008	0.011
13	500	0.000	0.001	0.005	0.006	0.009
14	510	0.000	0.000	0.004	0.005	0.007
15	520	0.000	0.000	0.002	0.004	0.005
16	530	0.000	0.000	0.003	0.003	0.004
17	540	0.000	0.000	0.000	0.001	0.002

* Concentration of 3-methyl-1-indanone taken each time is $3.84 \times 10^{-3}\text{M}$ Figure 1. Absorption spectra of 3-methyl-1-indanone ($3.84 \times 10^{-3}\text{M}$) in presence of varying amounts of SnCl_4 using o -dichlorobenzene as solvent.

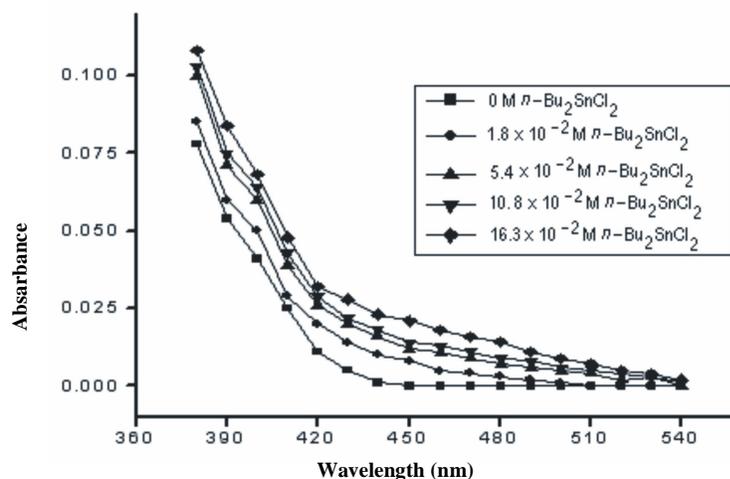


Figure 2. Absorption spectra of 3-methyl-1-indanone (3.84×10^{-3} M) in presence of varying amounts of $n\text{-Bu}_2\text{SnCl}_2$ using *o*-dichlorobenzene as solvent.

Table 3. Concentration and absorption data of the ligand with SnCl_4

Conc. of SnCl_4	Absorption at 430 nm	D- D_0	$[\text{SnCl}_4] / \text{D}-D_0$	1/D
1.86×10^{-3} M	0.202	0.185	10.05×10^{-3}	4.950
3.73×10^{-3} M	0.260	0.243	15.35×10^{-3}	3.850
7.45×10^{-3} M	0.310	0.293	25.43×10^{-3}	3.230
14.91×10^{-3} M	0.292	0.375	39.76×10^{-3}	2.550

Concentration of indanone (base) = 3.84×10^{-3} M

Absorption of pure indanone solution at 430 nm = $D_0 = 0.017$

Relation:- $[\text{SnCl}_4] / \text{D}-D_0 = -1/\text{K} \times 1/\text{D} + 1/\text{KD}_\infty$

Where

D_0 = Absorption of pure indanone solution

D = Absorption at a given concentration of alkyltin halide

D_∞ = Absorption for complete adduct formation

K = Equilibrium constant

From graph (Fig. 3) K = 69.7

Table 4. Concentration and absorption data of the ligand with *n*-Bu₂SnCl₂.

Conc. of Bu ₂ SnCl ₂	Absorption at 420 nm	D-D ₀	[Bu ₂ SnCl ₂] / D-D ₀	1/D
$1.81 \times 10^{-2} \text{M}$	0.020	0.009	2.640	50.00
$5.44 \times 10^{-2} \text{M}$	0.026	0.015	3.630	38.46
$10.87 \times 10^{-2} \text{M}$	0.029	0.018	5.040	34.48
$16.31 \times 10^{-2} \text{M}$	0.033	0.022	7.410	30.30

Concentration of indanone (base) = $3.84 \times 10^{-3} \text{M}$

Absorption of pure indanone solution at 420 nm = $D_0 = 0.011$

Relation:- $[n\text{-Bu}_2\text{SnCl}_2] / D - D_0 = -1/K \times 1/D + 1/KD_\infty$

From graph (Fig. 4) $K = 4.6$

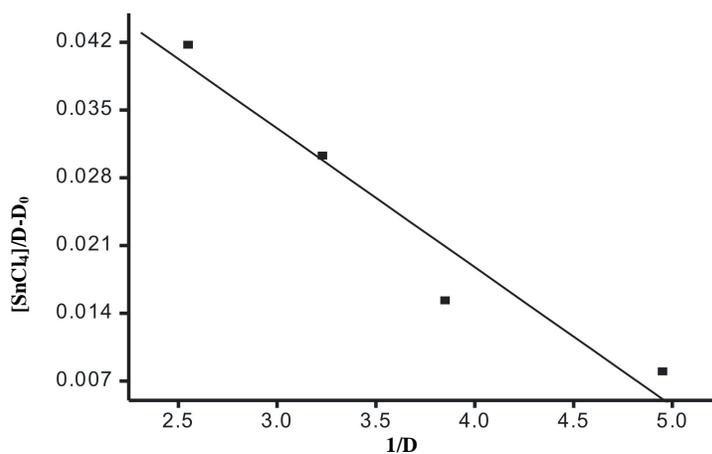


Figure 3. Plot of $[\text{SnCl}_4]/D - D_0$ Vs $1/D$ for the interaction of 3-methyl-1-indanone with SnCl_4 .

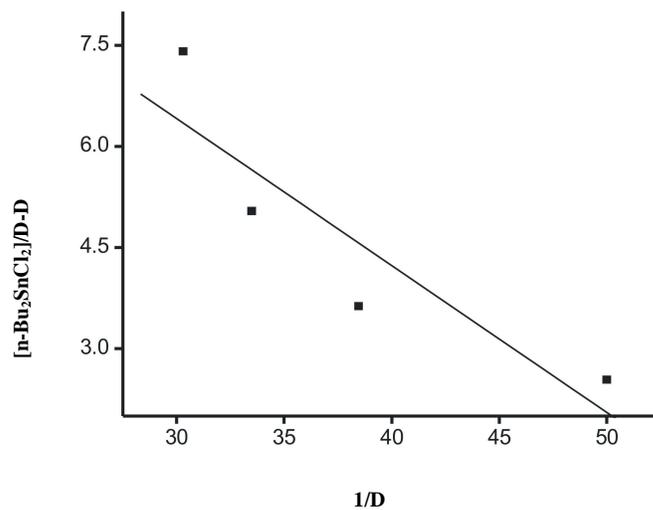


Figure 4. Plot of $[n\text{-Bu}_2\text{SnCl}_2]/D - D_0$ Vs $1/D$ for the interaction of 3-methyl-1-indanone with $n\text{-Bu}_2\text{SnCl}_2$.

the absorption increased. Absorption maxima were observed at 430 and 380 nm for SnCl_4 and $n\text{-Bu}_2\text{SnCl}_2$ respectively. Further increase in SnCl_4 or $n\text{-Bu}_2\text{SnCl}_2$ concentration was not possible experimentally because of weaker interaction between ketone and tin moieties. Attempts are made to calculate the equilibrium constant for the adduct formation between SnCl_4 or Bu_2SnCl_2 with 3-methyl-1-indanone and the results are shown in Tables 3 and 4. A plot of $[\text{SnCl}_4]/D\text{-}D_0$ and $n\text{-Bu}_2\text{SnCl}_2/D\text{-}D_0$ against $1/D$ gave a straight line (Fig. 3 and 4).

The equilibrium constant K found from the plot shown in Figs. 3 and 4 is 69.7 for SnCl_4 and 4.6 for $n\text{-Bu}_2\text{SnCl}_2$. These results show that 3-methyl-1-indanone interacts with SnCl_4 or $n\text{-Bu}_2\text{SnCl}_2$ in the aprotic medium and the interaction is reversible. The compound formed in solution has a 1:1 stoichiometry.

The equilibrium constant values show that SnCl_4 is about fourteen times stronger acid than $n\text{-Bu}_2\text{SnCl}_2$. It can be explained on the basis of replacement of two chloro- groups by butyl groups. This dictates that presence of highly electronegative group on tin increases its Lewis acidity.

References

1. Mc Graw Hill Encyclopedia of Science and Technology, Mc Graw Hill, New York 18 (1987) 367-369.
2. William Benton, *Encyclopedia Britannica*, London, 9 (1997) 1019-1021.
3. S. Tsunoi, H. Shioji and M. Tanika, *Analytical Sciences*, 20 (2004) 101.
4. P. Novak, I. Gisurora, R. Jamber, A. Ruzicka & J. Holecek, *Appl. Organometal. Chem.*, 18 (2004) 241.
5. W. Rehman, M.K. Baloch, B. Muhammad, A. Badshah and K. M. Khan, *Chinese Sci. Bull.*, 49 (2004) 119.
6. I. Din, M. Mazhar, K. M. Khan, M.F Mohan, K.C. Molloy, *J. Organomet. Chem.*, 689 (2004) 899.
7. M. Danish, H. G. Alt, A. Badshah, S. Ali, M. Mazhar and N. Islam, *J. Organomet. Chem.*, 486 (1995) 51.
8. M. Danish, S. Ali, M. Mazhar, A. Badshah, M. I. Chaudhry, H.G. Alt and G. Kehr, *Polyhedron*, 14 (1995) 3115.
9. M. Danish, S. Ali, M. Mazhar, and A. Badshah, *Main Group Metal Chem.*, 19 (1996) 121.
10. M. Danish, S. Ali, M. Mazhar, A. Badshah and E.R.T. Tiekink, *Main Group Metal Chem.*, 18 (1995) 617.
11. M. Danish, S. Ali, M. Mazhar, T. Masood and E.R.T. Tiekink, *Main Group Metal Chem.*, 18 (1995) 27.
12. M. Danish, S. Ali, and M. Mazhar, *Heteroatom Chem.*, 7 (1996) 233.
13. C. M. Ashraf, W.R. Jackson and D. Rosh, *Aust. J. Chem.*, 28 (1975) 197.
14. C. M. Ashraf and W. R. Jackson, *Aust. J. Chem.*, 31 (1978) 1845.
15. C. M. Ashraf, *Arab Gulf J. Scient. Res. Math. Phys. Sci.*, A5 (1987) 11.
16. D. D. Perrin and W. L. F. Armergo, "Purification of Laboratory Chemicals" ed 3rd, Pergamon, Oxford, (1987).
17. F. Koelsch, H. Hockmann and C.D. Claire, *J. Am. Chem. Soc.*, 65 (1943) 59.