Asian Journal of Chemistry Vol. 8, No. 4 (1996), 586–588

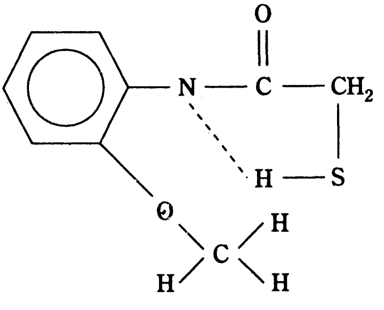
Physico-Chemical Studies of σ-bonded complexes of Dialkyltin(IV) Cations with N-(*o*-anisyl) and N-(*p*-anisyl)-2-Mercaptoacetamides

GATTU S. RATHOUR and PUSHPA BHAGCHANDANI*
Department of Chemistry
Sanatan Dharam Government College
Beawar-305 901, India

In the present work, a comparative study of the stability constants of σ-bonded dialkyltin(IV) cations with N-(*o*-anisyl) and N-(*p*-anisyl)-2-mercaptoacetamide have been described.

INTRODUCTION

The comparison of successive stability constants of the complexes of N-(*o*-anisyl)-2-merceptoacetamides and N-(*p*-anisyl)-2-mercaptoacetamides with the various σ-bonded dialkyltin(IV) cations have been determined in dioxane-water mixture (75%, v/v) at 30 ± 0.1°C and at constant ionic strength $\mu = 0.1$ M (NaCl) by adopting the pH-titration technique of Irving and Rossotti.[1]



N-(*o*-anisyl)-2-mercaptoacetamide

EXPERIMENTAL

All the chemicals used were of AR grade. Several methods are available for the preparation of N-(*o*-anisyl)-2-mercaptoacetamide and N-(*p*-anisyl)-2-mercaptoacetamide.[3,4] Regarding efficiency of the yield Sircar method[5] is the best and this was used for preparation of the above ligands. Dioxane was purified by a standard procedure.[6] Dioxane-water (75%, v/v) was used in preparing metal salt, ligand and NaCl solutions.

The pH-titrations were performed with an ECIL-823 pH-meter using glass electrode and a saturated calomel electrode (SCE). Titrations were performed in a titration cell maintained at 30 ± 0.1°C. The electrodes were calibrated using potassium hydrogen phthalate (pH = 4) and borate buffer (pH = 9.27) and checked before and after each titration. Two sets of titrations were performed, one with the ligand solution and the other with the ligand solution containing dialkyltin dichloride. Change in pH was recorded as a function of the volume of NaOH added.

The following solutions were used:

(i) 10 mL of 0.05 M ligand + 20 mL of 0.25 M NaCl + 19.5 mL of dioxane-water mixture (75%, v/v), and

(ii) 10 mL of 0.05 M ligand + 10 mL of 0.0125 M dialkyltin dichloride + 20 mL of 0.25 M NaCl + 10 mL of dioxane-water (75%, v/v).

In the first set of titrations the titrant NaOH was of strength 0.5 M, whereas in the second set of titrations the strength of NaOH was 0.1 M.

RESULTS AND DISCUSSION

By comparison of curves from the pH titration the values of $\bar{n}_a$ (the average number of protons attached per ligand molecule), $\bar{n}$ (the average number of ligand ions attached per metal ion), and pL (free ligand exponent) were obtained adopting the Irving-Rossotti technique[1]. Various methods (interpolation at half $\bar{n}$ value, least-square method and correction term method) were used to compute stability constants.

The comparison of the values obtained by different methods shows that these are in good agreement with each other. The average values are reported in Table-1.

TABLE
COMPARISON OF STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES.

Temperature = 30 + 0.1°C μ = 0.1M NaCl Solvent: Dioxane-water mixture (75% v/v).

Metal	Interpolation at half $\bar{n}$ values			Correction term method			Least square method		
	$\log k_1$	$\log k_2$	$\log \beta_2$	$\log k_1$	$\log k_2$	$\log \beta_2$	$\log k_1$	$\log k_2$	$\log \beta_2$
				(p-$OCH_3C_6H_4$)$NHCOCH_2SH$					
A	19.25	9.24	28.49	14.20	9.26	23.46	14.22	9.22	23.42
B	14.24	9.14	23.38	14.18	9.15	23.33	14.12	9.14	23.26
C	14.24	8.98	23.32	14.16	8.98	23.14	14.18	9.04	23.22
				(o-$OCH_3C_6H_4$)$NHCOCH_2SH$					
A	12.83	8.47	21.30	12.83	8.47	21.30	12.79	8.51	21.30
B	12.78	8.16	20.94	12.74	8.13	20.87	12.75	8.14	20.89
C	12.78	7.92	20.70	12.75	7.86	20.61	12.79	7.81	20.60

A = $(CH_3)_2SnCl_2$, B = $(C_3H_5)_2SnCl_2$, C = $(n\text{-}C_4H_9)_2SnCl_2$

The maximum value of $\bar{n}$ obtained in the pH region, where hydrolysis of metal ion is negligible, is between 1.5 and 2.0, which reveals that metal-ligand ratio in the complexes is 1 : 2. A comparison of log β_2 values reveals the following order of metal chelate stabilities

$$(CH_3)_2SnCl_2 > (C_2H_5)_2SnCl_2 > (n\text{-}C_4H_9)_2SnCl_2$$

which is in conformity with the Irving-Williams order[2].

On comparing the log β_2 values of N-(*o*-anisyl)-2-mercaptoacetamide and N-(*p*-anisyl)-2-mercaptoacetamide one finds that the former is a stronger acid than the latter.

Although the methoxy group attached, respectively, at the *o*- and *p*- positions of the phenyl ring in the above compounds exhibits both +M and +I effects, the extent of intermolecular hydrogen bonding between the nitrogen lone pair and sulphydryl hydrogen is more sterically hindered by the *o*-CH_3 substituent in N-(*o*-anisyl)-2-mercaptoacetamide rather than in N-(*p*-anisyl)-2-mercaptoacetamide.

REFERENCES

1. H.M Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
2. H.M. Irving and R.J.P. William, *J. Chem. Soc.*, 3206 (1953).
3. H.Beckurts and H. Fresichs, *J. Pract. Chem.*, **66**, 1092 (1974).
4. J.A. van Allan, *J. Am. Chem. Soc.*, **69**, 2914 (1946).
5. R.N. Mishra and S.S. Guha Sircar, *J. Indian Chem. Soc.*, **32**, 127 (1955).
6. A.I. Vogel, A Text Book of Practical Organic Chemistry, 3rd Ed., Longmans, London (1971).

(*Received:* 10 October 1995; *Accepted:* 20 May 1996) AJC-1099