

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Formation Constant of Dialkyltin(IV)-N-(Alkyl)-2/3-mercaptoacetamide Systems

B. P. Bachlas^a; S. K. Gupta^a; S. C. Shukla^a; T. S. Kapoor^a

^a Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Bachlas, B. P. , Gupta, S. K. , Shukla, S. C. and Kapoor, T. S.(1984) 'Formation Constant of Dialkyltin(IV)-N-(Alkyl)-2/3-mercaptoacetamide Systems', *Journal of Macromolecular Science, Part A*, 21: 5, 555 – 560

To link to this Article: DOI: 10.1080/00222338408056572

URL: <http://dx.doi.org/10.1080/00222338408056572>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Formation Constant of Dialkyltin(IV)- N-(Alkyl)-2/3-mercaptoacetamide Systems

B. P. BACHLAS,* S. K. GUPTA, S. C. SHUKLA, and T. S. KAPOOR

Department of Chemistry
University of Rajasthan
Jaipur 302004, India

ABSTRACT

The thermodynamic formation constants of N-(alkyl)-2- and/or 3-mercaptoacetamides complexes with dimethyl-, diethyl-, and n-dibutyltin(IV) cations have been determined potentiometrically in a dioxane-water mixture (75% v/v) at $30 \pm 0.1^\circ\text{C}$ in $\mu = 0.1\text{ M}$ NaCl using the Irving-Rossotti method and refined by the least-squares method. The basicity of the ligands follows the order $\text{C}_2\text{H}_5\text{NHCOCH}_2\text{SH} > n\text{-C}_3\text{H}_7\text{NHCOCH}_2\text{SH} > n\text{-C}_4\text{H}_9\text{NHCOCH}_2\text{SH} > \text{C}_2\text{H}_5\text{NHCOCH}_2\text{CH}_2\text{SH} > n\text{-C}_3\text{H}_7\text{NHCOCH}_2\text{CH}_2\text{SH} > n\text{-C}_4\text{H}_9\text{NHCOCH}_2\text{CH}_2\text{SH}$. For each ligand the stability order of dialkyltin(IV) complexes decreases as follows: $[\text{Me}_2\text{Sn(IV)}]^{2+} > [\text{Et}_2\text{Sn(IV)}]^{2+} > [n\text{-Bu}_2\text{Sn(IV)}]^{2+}$. This order is consistent with the group electronegativities of $[\text{R}_2\text{Sn(IV)}]^{2+}$ cations calculated from Sanderson's electronegativity scale.

*To whom correspondence should be addressed.

INTRODUCTION

The effect of alkyl group on the electron acceptor and acid strength of di- and trialkyltin(IV) compounds has been a subject of numerous investigations [1-5]. A survey of the literature reveals that very little has been reported about the formation constants of dialkyltin(IV)-N-(alkyl)-2- and/or 3-mercaptoacetamide systems [5, 6].

EXPERIMENTAL

N-(Alkyl)-2-mercaptoacetamides and N-(alkyl)-3-mercapto-propionamides were prepared by a standard procedure [7]. Dioxane was dried and purified by a literature method [8]. Other experimental conditions were described earlier [5, 6].

Prior to precipitation, changes in pH were recorded as a function of volume of titrant added. Oxygen-free nitrogen gas was passed continuously through the reaction cell in order to prevent any oxidation during the titrations.

The (\bar{n}_A) values of the titled ligands together with k_1 , k_2 , and β_2 were calculated by the Irving-Rossotti method [9] and the raw data processed by the least-squares method [10] (Table 1).

The formation constants data were converted into thermodynamic values by the formula of Rao and Mathur [11] (Table 2).

TABLE 1. Ligand Anion-Proton Stability Constants of N-(Alkyl)-2- and/or 3-mercaptoacetamides

Ligand	$\bar{n}_{\text{NH}_2^+}$	\bar{n}_{SH}	\bar{n}_{NH}
$\text{C}_2\text{H}_5\text{NHCOCH}_2\text{SH}$	~2.0	9.40	12.52
$n\text{-C}_3\text{H}_7\text{NHCOCH}_2\text{SH}$	~2.0	9.02	11.90
$n\text{-C}_4\text{H}_9\text{NHCOCH}_2\text{SH}$	~2.0	8.10	11.27
$\text{C}_2\text{H}_5\text{NHCOCH}_2\text{CH}_2\text{SH}$	~2.5	7.87	12.15
$n\text{-C}_3\text{H}_7\text{NHCOCH}_2\text{CH}_2\text{SH}$	~2.5	7.55	11.52
$n\text{-C}_4\text{H}_9\text{NHCOCH}_2\text{CH}_2\text{SH}$	~2.5	7.08	11.10

TABLE 2. Thermodynamic Stepwise and Overall Formation Constants of Dialkyltin(IV)-N-(alkyl)-2- and/or 3-mercaptoacetamide Systems

$R_2Sn(IV)^{2+}$ R =	Irving-Rossotti method			Least-squares method		
	$\log k_1$	$\log k_2$	$\log \beta_2$	$\log k_1$	$\log k_2$	$\log \beta_2$
	<u>$C_2H_5NHCOCH_2SH$</u>					
Me	11.70	4.43	16.13	11.72	4.43	16.15
Et	11.48	4.39	15.87	11.48	4.36	15.84
n-Bu	11.22	4.35	15.57	11.20	4.33	15.53
	<u>$n-C_3H_7NHCOCH_2SH$</u>					
Me	11.38	4.46	15.84	11.44	4.44	15.88
Et	11.15	4.42	15.57	11.15	4.38	15.53
n-Bu	11.01	4.37	15.38	11.01	4.39	15.40
	<u>$n-C_4H_9NHCOCH_2SH$</u>					
Me	11.17	4.29	15.46	11.17	4.24	15.41
Et	11.10	4.27	15.37	11.10	4.22	15.32
n-Bu	11.00	4.26	15.26	11.01	4.21	15.26
	<u>$C_2H_5NHCOCH_2CH_2SH$</u>					
Me	10.00	4.44	14.44	10.02	4.34	14.36
Et	9.93	4.34	14.27	9.87	4.31	14.18
n-Bu	9.88	-	-	-	-	-
	<u>$n-C_3H_7NHCOCH_2CH_2SH$</u>					
Me	9.45	4.31	13.76	9.43	4.29	13.72
Et	9.40	4.28	13.68	9.36	4.26	13.62
n-Bu	9.36	-	-	-	-	-
	<u>$n-C_4H_9NHCOCH_2CH_2SH$</u>					
Me	8.90	4.13	13.03	8.92	4.04	12.96
Et	8.83	4.06	12.89	8.85	3.96	12.81
n-Bu	8.80	-	-	-	-	-

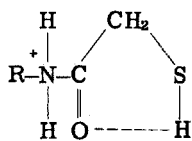
RESULTS AND DISCUSSION

N-(Alkyl)-2- and/or 3-mercaptoacetamides show a pronounced tendency to protonate at the secondary nitrogen atom when mineral acid (HCl) is added to the ligand solution, and they are independent of the nature of the N-alkyl substituent. However, \bar{n}_{SH} and \bar{n}_{NH} vary with the nature of the alkyl group.

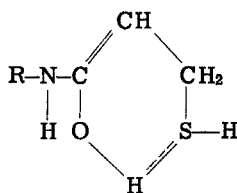
A solution of N-(alkyl)-2- and/or 3-mercaptoacetamide containing an adequate amount of hydrochloric acid is titrated with sodium hydroxide. Excess acid is titrated first, prior to the elimination of the proton attached to the secondary nitrogen, and subsequently the proton of the sulfhydryl group is removed. From Table 1 it can be seen that the removal of the -SH proton occurs around pH 8.10-9.40 in the case of N-(alkyl)-2-mercaptoacetamides and 7.08-7.87 in the case of N-(alkyl)-3-mercaptoacetamides. At a higher pH, say, around 11.27 to 12.52, the hydrogen originally bound to the secondary nitrogen ionizes as a proton in the case of N-(alkyl)-2-mercaptoacetamides and 11.10 to 12.15 in the case of N-(alkyl)-3-mercaptoacetamides. This is because of the fairly high bond strength of the N-H bond relative to the S-H bond. Therefore, the -SH group is regarded as more acidic than the -NH group. Further $\bar{n}_{NH_2^+}$ values lie between 2.0 to 2.5 for N-(alkyl)-2- and/or 3-mercaptoacetamides.

On the basis of \bar{n}_A values, the order of basicity of ligands of both series is $C_2H_5 > n-C_3H_7 > n-C_4H_9$.

The magnitude of \bar{n}_A values indicates that unlike N-(alkyl)-2-mercaptoacetamides, N-(alkyl)-3-mercaptoacetamides are stronger acids. This can be explained on the basis of the following two structures for the protonated species of the above two classes of compounds.



(I)



(II)

In structure I the -SH group is held more firmly by the carbonyl oxygen through intramolecular hydrogen bonding, while in Structure II the sulfhydryl hydrogen is free although the sulfur of the sulfhydryl group is engaged in hydrogen bonding with the -OH group.

An inspection of the thermodynamic formation constants in Table 2 shows that N-(alkyl)-2-mercaptoacetamide ligands form stronger complexes with dialkyltin cations in comparison to N-(alkyl)-3-mercapto-

propionamide ligands. Except for *n*-dibutyltin(IV)-*N*-(alkyl)-3-mercaptopropionamide systems, the composition of complexes in both the systems was found to be 1:2. Within the dialkyltin(IV) cation series, the following sequence in the decreasing order of their overall thermodynamic formation constants has been observed: $[\text{Me}_2\text{Sn}(\text{IV})]^{2+} > [\text{Et}_2\text{Sn}(\text{IV})]^{2+} > [\text{n-Bu}_2\text{Sn}(\text{IV})]^{2+}$. This order is consistent with the group electronegativities of $[\text{R}_2\text{Sn}(\text{IV})]^{2+}$ cations calculated by the Sanderson method [5]. The group electronegativity of the $[\text{R}_2\text{Sn}(\text{IV})]^{2+}$ cation decreases from dimethyltin to diethyltin and further decreases to *n*-dibutyltin(IV) cations. The decrease in electronegativities has been justified on the basis of an increase in the inductive effect (+I) of the alkyl group from methyl to ethyl and *n*-butyl, and a decrease in the partial charge at the central tin(IV) atom.

Further, dialkyltin(IV) cations form stronger complexes with *N*-(ethyl)- than with *N*-(*n*-propyl)-, and this in turn forms stronger complexes with *N*-(*n*-butyl)-2- and/or 3-mercaptoacetamides. This can be explained on the basis of the basicity of the ligands and the interplay of steric hindrance due to the alkyl group substituents attached to the secondary nitrogen atom as well as on the tin(IV) atom. From the magnitude of $\log \beta_2$ it is clear that dialkyltin(IV) cations show a soft character [12], thereby forming stronger complexes because of $d\pi-p\pi$ bonding with these sulfur ligands.

ACKNOWLEDGMENT

The authors are thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur, for providing the necessary facilities.

REFERENCES

- [1] R. S. Tobias, Organometal. Chem. Rev., **1**, 93 (1966).
- [2] E. G. Rochow and D. Seyferth, J. Am. Chem. Soc., **45**, 3078 (1953).
- [3] R. H. Prince, J. Chem. Soc., p. 1783 (1959).
- [4] R. S. Tobias and B. A. Nevett, Chem. Ind., p. 40 (1963).
- [5] S. K. Gupta and B. P. Bachlas, Egypt. J. Chem., **21** (1981).
- [6] S. K. Gupta, Y. Maire, and B. P. Bachlas, Acta Cienc. Indica, **7C**(1), 91 (1981).
- [7] C. S. Bhandari, PhD Thesis, University of Rajasthan, Jaipur, India, 1969.
- [8] A. I. Vogel, A Text Book of Practical Organic Chemistry, 3rd ed., Longmans, London, 1969.
- [9] H. M. Irving and H. S. Rossotti, J. Chem. Soc., p. 2904 (1954).

- [10] H. M. Irving and H. S. Rossotti, Ibid., p. 3397 (1953).
- [11] B. Rao and H. B. Mathur, J. Inorg. Nucl. Chem., 33, 2919 (1971).
- [12] S. Ahrland, J. Chatt, and N. R. Davies, Q. Rev., 12, 265 (1958).

Accepted by editor August 30, 1983

Received for publication September 30, 1983