Inorganica Chimica Acta, *90* (1984) 53–56

Spectrophotometric Studies on Complexes Formed between Tri-, Di- and Monobutyltin(IV) Chlorides and 3-Hydroxyflavone in Different Solvents

WENCHE LANGSETH

Department of Chemistry, University of Oslo, Oslo 3, Norway

Received March 3, 1984

The complex formation of tri-, di- and monobutyltin(IV) chloride with 3-hydroxyflavone was studied spectrophotometrically in methanol, chloroform and toluene (the last two after extraction with buffer pH 9.0) by the molar ratio method. The composition of the chelates formed was found to be solvent and molar ratio (C_M/C_L) dependent. The complex formation constants were calculated.

Introduction

3-Hydroxyflavone has been used as an analytical reagent for the determination of inorganic [1] and organic tin compounds [2–5]. Examination of the structures has been done [6]. Better information about the complexes in solution is needed however, when for instance metals are determined as chelates using high-performance liquid chromatography [7]. Studies of the absorption of visible and ultraviolet radiation have long been used to obtain information on the composition of a complex in solution.

This paper describes complexes formed between tri-, di- and monobutyltin chloride and 3-hydroxyflavone in solution. The solvents methanol, chloroform and toluene, which have different polarity and solvent properties, were chosen for the present study, chloroform and toluene being extracted with buffer of pH 9.0.

Experimental

Reagents

Chemicals were obtained from the following sources: tri- and dibutyltin chloride from Fluka AG (Switzerland); monobutyltin chloride from ICN Pharmaceuticals, K & K, Rare and Fine Chemicals (New York) and 3-hydroxyflavone from Eastman Kodak Ltd.

Tri- and monobutyltin chloride were purified by distillation. Dibutyltin dichloride was recrystallized from light petroleum (boiling range 40–60 °C). 3-Hydroxyflavone was used directly without further purification.

Boric Acid Buffer

The buffer was made according to the procedure given in an earlier paper [8]. Boric acid (3.1 g, 0.05 *M*) and sodium perchlorate monohydrate (140 g, 1.0 *M*) were dissolved in water to 1.0 l solution. pH was adjusted with sodium hydroxide pellets to 9.0.

Apparatus

UV/visible spectra were recorded on a Cary 14 spectrophotometer, while measurements taken at a special wavelength were made with a Cary 16 spectrophotometer.

Procedure

The butyltin chlorides and 3-hydroxyflavone were dissolved separately in the organic solvents. Various amounts of butyltin chloride and 3-hydroxyflavone were added to 10 ml volumetric flasks when using methanol, or separation funnels containing 10 ml of buffer solution when using chloroform and toluene. The total volume of organic solvent was adjusted to 10 ml. When extracting with buffer solution the separation funnel was shaken vigorously for 2 min. After separation the absorbance of the organic layer was measured in 1 cm cells at about 390 nm. The concentration of 3-hydroxyflavone when measuring the molar absorptivity against molar ratios were 6.00×10^{-5} *M* with tributyltin chloride and 4.00×10^{-5} *M* with di- and monobutyltin chloride. When measuring the molar absorptivities in excess of ligand the concentration was ten times higher.

UV/visible spectra of all the systems for different molar ratios were taken. It was also examined whether the wavelength of maximum absorbance was molar ratio dependent. Generally the UV spectra were very similar for the different butyltin complexes examined.

The Molar Ratio Method

This work is based on the use of the molar ratio method [9, 10]. The ligand concentration was kept

0020-1693/84/$3.00

TABLE I. Molar Absorptivities and Complex Formation Constants of Butyltin–3-Hydroxyflavone Complexes Determined by the Molar Ratio Method.*

Organotin Chloride	Solvent	λ_{max}	ϵ_1 (10^4 mol^{-1} cm^{-1})	ϵ_2	ϵ_3	K_1	K_2	K_3	s^a
3-OH-flavone	MeOH	344	1.65						
Bu_3SnCl	MeOH	398	1.55			3.8×10^3			0.034
Bu_3SnCl	$CHCl_3$	387	1.68			2.7×10^4			0.011
Bu_3SnCl	Toluene	387	1.67			9.0×10^5			0.040
Bu_2SnCl_2	MeOH	398	1.68	3.54		3.8×10^5	1×10^{10}		0.007
Bu_2SnCl_2	$CHCl_3$	387		3.57			6×10^{10}		0.023
Bu_2SnCl_2	Toluene	387		3.49			8×10^{10}		0.010
$BuSnCl_3$	MeOH	396		4.87^b			9×10^9		0.035
				4.18^c			5×10^{10}		0.041
$BuSnCl_3$	$CHCl_3$	402	1.68	3.57	4.49	5.6×10^3	5×10^6	2×10^{13}	0.018
				4.49^c			3×10^8		0.048
$BuSnCl_3$	Toluene	400(393)	1.68	3.49	4.49	2.2×10^3	3×10^7	2×10^{13}	0.015
				4.69^c			4×10^8		0.042

*ϵ_1, ϵ_2 and ϵ_3 are the molar absorptivities of 1:1, 1:2 and 1:3 complexes, respectively, and K_1, K_2 and K_3 their respective complex formation constants. [a]Standard deviation (see text for further information). [b]Best calculated value. [c]Measured value.

constant while changing the metal concentration. Measurements were taken at the wavelength of the absorbance maximum of the complex.

The molar absorptivities were measured in the presence of an excess of 3-hydroxyflavone. In some cases more than one species were formed with the same solvent. Usually the absorptivity of the 1:1 complex, if formed, could be determined from maximum absorbance of the molar plot, A_{max}. Otherwise values obtained with other solvents for the same complexes had to be used. Calculations showed that except for tributyltin in methanol and chloroform, the error of assuming that the measured absorptivity in excess of ligand belonged to the complex of highest ligand content formed, was less than one percent. In the case of tributyltin in methanol the degree of complex formation was too low for measurement of the molar absorptivity in excess of 3-hydroxyflavone. About six percent of tributyltin was not present as a complex in chloroform.

The absorbance measured at a given wavelength is

$$A_x = \Sigma(\epsilon_n \cdot [Bu_xSnCl_{(4-x-n)}of_n]) + \epsilon_L \cdot [Hof] + A_{bl}$$

where ϵ_n is the molar absorptivity of the complex $Bu_xSnCl_{(4-x-n)}of_n$ (of = 3-hydroxyflavonate), ϵ_L the absorptivity of 3-hydroxyflavone and A_{bl} the absorbance of the blank solution containing neither the butyltin chloride nor the ligand, at the wavelength of measurement. Butyltin chlorides have no absorbance at these wavelengths. The sample path length was 1 cm.

Complexes between butyltin chlorides and 3-hydroxyflavone were assumed to contain only one organometallic group and to be monomeric in solution. The equation of complex formation at equilibrium is then

$$n \cdot Hof + Bu_xSnCl_{(4-x)} \rightleftharpoons Bu_xSnCl_{(4-x-n)}of_n + n \cdot HCl$$

The complex formation constants given in this paper are calculated according to the equation

$$K_n = \frac{[Bu_xSnCl_{(4-x-n)}of_n]}{[Bu_xSnCl_{(4-x)}]\,[Hof]^n}$$

where the index n in K_n gives the number of 3-hydroxyflavone groups bound to butyltin.

Further comments are given in [8].

Results and Discussion

Molar absorptivities and complex formation constants determined by the molar ratio method are given in Table I.

Tributyltin chloride is found from the molar ratio curves to form 1:1 complexes with 3-hydroxyflavone

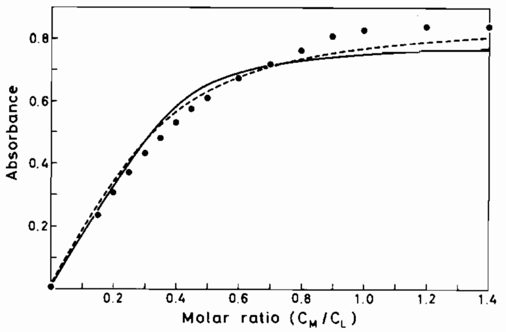

Fig. 1. Molar ratio plot of monobutyltin trichloride in methanol. ● measured values; ——— calculated curve when $\epsilon_2 = 4.18 \times 10^4$; ------ calculated curve when $\epsilon_2 = 4.89 \times 10^4$.

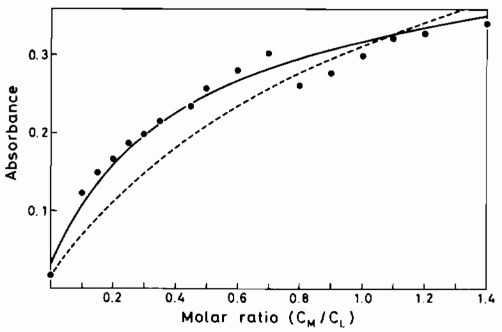

Fig. 2. Molar ratio plot of monobutyltin trichloride in chloroform. ● measured values. ——— calculated curve when K_1, K_2 and K_3 are set different from zero; ------ calculated curve when only K_2 is set different form zero ($K_1 = 0, K_2 = 0$).

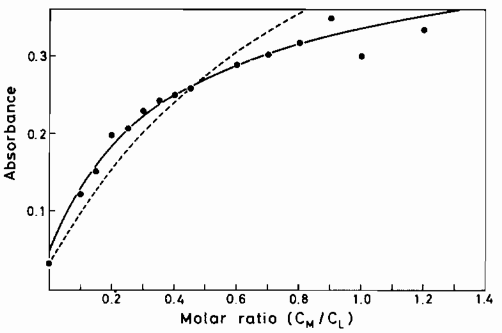

Fig. 3. Molar ratio plot of monobutyltin trichloride in toluene. ● measured values; ——— calculated curve when K_1, K_2 and K_3 are set different form zero; ------ calculated curve when only K_2 is set different form zero ($K_1 = 0$, $K_2 = 0$).

in all three solvent systems, according to the results observed for triorganotin compounds [6]. The absorptivity in excess of ligand in methanol has not been obtained. But assuming the same value as measured in toluene, acceptable correspondence between experimental and calculated molar ratio curves was achieved for all three solvent systems.

Dibutyltin dichloride forms a 1:2 complex with 3-hydroxyflavone using chloroform or toluene as solvent.

Good correspondence between experimental and calculated molar ratio curves in methanol however is only achieved if both Bu_2Snof_2 and $Bu_2SnClof$ (Hof = 3-hydroxyflavone) are assumed to be formed. The measured absorptivity in excess of ligand, 2.06×10^4, is higher than for Bu_3Snof but is much lower than those achieved for Bu_2Snof_2 in chloroform and toluene. The molar ratio plots approach A_{max} very slowly. The methanol solution also shows quite intense violet fluorescence in excess of dibutyltin dichloride, which is in agreement with other workers' observations for comparable systems [3, 6]. The fluorescence of organotin complexes of 3-hydroxyflavone has been connected with the penta-coordination of the tin atom. The formation of $Bu_2SnClof$ for high concentration of dibutyltin dichloride in methanol solution is supported by these observations.

Less predictable results are observed for butyltin trichloride. The measured absorptivities are much higher than those found for Bu_2Snof_2.

In methanol the absorbance measured in excess of butyltin trichloride, 4.18×10^4, predicts an absorptivity per ligand higher than those achieved for Bu_3Snof and Bu_2Snof_2. If complexes of the form ML, ML_2 and ML_3 are assumed to be the only alternatives, calculations predict the formation of a 1:2 complex between butyltin trichloride and 3-hydroxyflavone, having an absorptivity equal to the measured one (See Fig. 1). The calculated molar ratio curve seems however to deviate systematically from the experimental one. The form of the curve may indicate the existence of more than one absorbing species. The fact that the solution fluoresces in excess of butyltin trichloride could be due to $BuSnCl_2of$. The reduced intensity observed for $Bu_2SnClof$ in methanol can be explained by the higher Lewis acid strength of mono- compared to dibutyltin compounds [6].

Some other complexes may be formed that are of a form other than ML, ML_2 and ML_3, which are the requirements for the calculations.

In chloroform and toluene the degree of complex formation is very low. The precision is rather poor for high concentration of butyltin trichloride (see Figs. 2 and 3). Calculations indicate the formation of all three complexes; $BuSnX_2of$, $BuSnXof_2$ and $BuSnof_3$. UV spectra show a splitting of the absorption band, which becomes less and which is moved towards lower value at high concentrations of butyltin trichloride. This indicates the existence of at least two different absorbing species.

Conclusion

Measurement of the absorptivities gave about the same values in all three solvent systems, especially in chloroform and toluene, for the same butyltin compound.

Complexes containing one of group have a molar absorptivity equal to that of neat 3-hydroxyflavone, $\epsilon_1 = 1.68 \times 10^4$, while the absorptivity of 1:2 complexes is 3.54×10^4.

The degree of complex formation is found to be highest in toluene and lowest in methanol for the tri- and dibutyltin complexes, the difference being largest for the tributyltin complex. The opposite is however found for monobutyltin complexes, which can be explained by a higher polarity of the complex, and less hydrophobic groups.

References

1 C. F. Coyle and C. E. White, *Anal. Chem.,- 29,* 1486 (1957).
2 F. Vernon, *Anal. Chim. Acta, 71,* 192 (1974).
3 S. J. Blunden and A. H. Chapman, *Analyst, 105,* 1266 (1978).
4 P. G. Baker, D. S. Farrington and R. A. Hoodless, *Analyst, 105,* 282 (1980).
5 W. N.Aldridge and B. W. Street, *Analyst, 106,* 60 (1981).
6 S. J. Blunden and P. J. Smith, *J. Organomet. Chem., 226,* 157 (1982).
7 B. R. Willeford and H. Veening, *J. Chromatogr., 251,* 61 (1982).
8 W. Langseth, *Inorg. Chim. Acta, 87,* 47 (1984).
9 J. H. Joe and A. L. Jones, *Ind. Eng. Chem. Anal. Ed., 16,* 111 (1944).
10 K. Momoki, J. Sekino, H. Sato and N. Yamaguchi, *Anal. Chem., 41,* 1286 (1969).