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Spectrophotometric Determination of Equilibrium Constants of Dimethyl and Dibutyltin(IV) Dichloride with *meso*–Tetraphenylporphyrins

S. Hooshmand, J.B. Ghasemi and H. Nikyar
K. N. Toosi University, Chemistry Department Tech., Tehran, Iran

Abstract

The interactions of Me_2SnCl_2 and Bu_2SnCl_2 with ß–di, tri– and tetra–brominated *meso*–tetraphenylporphyrins, and *meso*–tetrakis(4–methylphenyl) and (4–methoxyphenyl) porphyrins, have been studied by the UV–Vis method. The different porphyrins form 1:1 adducts with Me_2SnCl_2 and Bu_2SnCl_2. The equilibrium constants of resulting complexes were calculated by using computer adjustment of UV–Vis spectrophotometry titration data with and mass balance and equilibrium constant equations. Refinement was carried out with a computer program, SQUAD. More refinement of the spectral data by multivariate curve resolutions approves 1:1 adducts formation.

Introduction

Molecular interactions of organotin(IV) halides with a variety of uni– and bidentate nitrogen donor ligands have been studied . Recently, more attention has concentrated on the antitumour properties of organotin(IV) halides, and a large number of studies have been made concerning the interactions of these compounds with biological systems. Studies of compounds of the type R_2SnX_2L, where L is a bidentate N-donor ligand showed that increasing stability is thought to reduce activity by hindering the dissociation of the ligand which is necessary for binding between tin and DNA. In view of these encouraging results, this led us to investigate the solution equilibria of organotin(IV) halide complexes with a number of free base *meso*–tetraphenylporphyrins. In the present work we investigated the formation constants for the interaction of dimethyl– and dibutyltin(IV) dichloride with H2TPP (*meso*–tetraphenylporphyrin), H_2TPPBr_4 (ß –Tetra–brominated *meso*–tetraphenylporphyrin), H_2TPPBr_3 (ß –Tri–brominated *meso*–tetraphenylporphyrin), H_2TPPBr_2 (ß –Di–brominated *meso*–tetraphenylporphyrin), $H_2T(4–CH_3)PP$ (*meso*–tetrakis(4–methylphenyl)porphyrin), and $H_2T(4–CH_3O)PP$ (*meso*–tetrakis(4–methoxyphenyl) porphyrin) in chloroform as a solvent.

Materials & Methods

Preparations: The free base *meso*–tetraphenylporphyrins was prepared and purified as reported previously [1–4].

General Method: UV–vis measurements(a Perkin Elmer (Lambda 25) spectrophotometer with 10 mm quartz cell) were carried out by a titration method at room temperature. In a typical measurement, 2.5 mL solution of each one of *meso* tetraphenylporphyrins (10^{-5}–10^{-6} M) in chloroform was titrated by R_2SnCl_2 (0.02 M). UV–Vis spectra were recorded over the range of 320–650 nm about 10 min after each addition. In this range of spectra, about 35–40 wavelengths that have suitable variations of absorbance were selected, and the formation constants of adduct formations were calculated. SQUAD program has been developed to enabling the evaluation of the best set of formation constant (K) of the proposed equilibrium model by employing a non–linear least–squares approach. The input data consist of (a) the absorbance values, (b) the total *meso* Tetraphenylporphyrins and Dimethyl and Dibutyltin(IV) Dichloride concentrations.

SQUAD is a program with a capability to refine the stability constants of a general complex, $M_mM_lH_kL_nL_q$, employing a non–linear least–squares approach. The data fed to SQUAD are the absorption spectra, chemical composition (total concentrations of M, M’, L, L’, and pH) and a chemical model to describe the system. The residual sum (U) is calculated from the following equation: $U=\Sigma_1^{I}\Sigma_1^{NW}(A_{i,k}^{calc}-A_{i,k}^{obs})^2$, where $A_{i,k}^{obs}$ is the absorbance value of the *i*th solution at the *k*th wavelength.

Results

Upon the addition of excess folds of R_2SnCl_2 (R = Me, Bu) to a solution of porphyrins in chloroform, the color changes to green. This change in color is due to the interactions of $R_2SnCl_2$with porphyrin.

Fig. 1 shows a typical titration spectra of H_2TPPBr_3 upon increasing addition of Me_2SnCl_2. Hypochromicity without any shift in Q–band were observed, which represents the existence of noncovalent interaction between R_2SnCl_2 and *meso*–Tetraphenylporphyrins complexes. The appearance of four simultaneous isosbestic points in porphyrines spectra clearly indicates the existence of simple equilibrium between free porphyrines and 1:1 porphyrin–R_2SnCl_2 complex. Upon the interaction of free base tetraphenylporphyrins with R_2SnCl_2 Lewis acids the original peaks of tetraphenylporphyrins (Soret band and Q bands) undergo considerable changes with a range of isosbestic points. For example by addition of Me_2SnCl_2 to H_2TPPBr_3, the original peaks of the free base were diminished and two new peaks appeared at 461 and 682 nm with isosbestic points around 371, 443, 503, 606 nm.

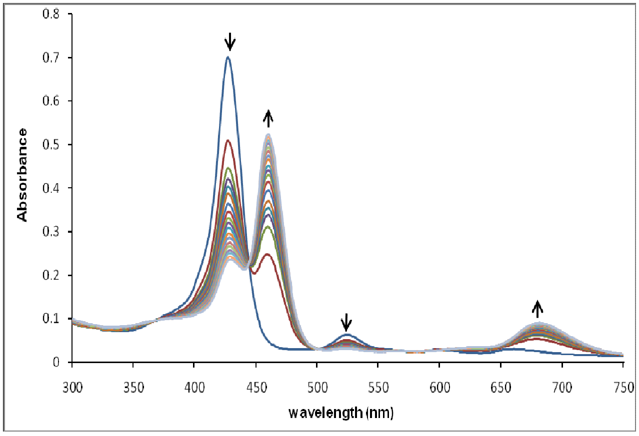

Figure 1; Spectral titration of H2TPPBr3 (2×10–6 M) with Me2SnCl2 (0.02 M) in chloroform.

The equilibrium constants were determined by analyzing the concentration and UV–Vis absorptions by the SQUAD program. These absorptions were analyzed by using the following mole ratios of the acid to base: (1) formation of the 1:1 adduct, (2) 2:1 adduct and (3) simultaneous formation of the 1:1 and 2:1 adducts. For the proposed models, formation of 1:1 adducts has the best fitting and the produced error sum of squares was between 10^{-2} and 10^{-3}. More refinement of the spectral data by MCR approves 1:1 adducts formation.

The results show that the 3quilibrium constants of the formed adducts from thermal titration, have an increasing trend from H_2TPPBr_3, H_2TPPBr_2, H_2TPP, $H_2T(4\text{–}CH_3)PP$, to $H_2T(4\text{–}CH_3O)PP$. For example, at 25 °C we have the following order of formation constants: Me_2SnCl_2–H_2TPPBr_4 < Me_2SnCl_2–H_2TPPBr_3 < Me_2SnCl_2–H_2TPPBr_2 < Me_2SnCl_2–H_2TPP < Me_2SnCl_2–$H_2T(4\text{–}CH_3)PP$ < Me_2SnCl_2–$H_2T(4\text{–}CH_3O)PP$. The corresponding formation constants are varied as 2.50 < 3.26 < 3.74 < 4.26 < 4.65< 4.83 respectively. On the other hand, we have greater stability constant for Me_2SnCl_2 reactions with respect to Bu_2SnCl_2's.

Conclusions

The refinement experimental data shows that the formation constants decreased with increasing number of bromide substitutes and increased with adding methyl and methoxy groups, as follow: $H_2T(4\text{–}CH_3O)PP > H_2T(4\text{–}CH_3)PP > H_2TPP > H_2TPPBr_2 > H_2TPPBr_3 > H_2TPPBr_4$ and $Me_2SnCl_2 > Bu_2SnCl_2$.

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