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Thermodynamic Studies of the Molecular Interactions of *p*-Halophenols with Free Bases *meso*-Tetraarylporphyrins

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The interactions of *p*-halophenols, *p*-BrC_6H_4OH and *p*-ClC_6H_4OH with free base *meso*-tetraphenylporphyrins ($H_2T(4\text{-}X)PP$; X= OCH_3, CH_3, H, Cl and $H_2T(3\text{-}X)PP$; X= CH_3, Cl) have been studied. The overall formation constants K (M^{-2}) and the thermodynamic parameters were calculated by using UV-Vis spectrophotometry titration. The overall formation constants show the following trend with X substituent of porphyrins: $H_2T(4\text{-}CH_3O)PP$ > $H_2T(3\text{-}Cl)PP$ > $H_2T(3\text{-}CH_3)PP$ > $H_2T(4\text{-}CH_3)P$ > H_2TPP > $H_2T(4\text{-}Cl)PP$ On the other hand, *p*-BrC_6H_4OH forms more stable adducts with free base porphyrins than *p*-ClC_6H_4OH.

Keywords: *p*-Halophenols, Free base porphyrins, Molecular adducts, Hydrogen-bonded complexes.

INTRODUCTION

The molecular interactions of tetraarylporphyrins with π-acceptor molecules, such as nitroaromatic systems[1–6], tetracyanoethylene[7] and 2,3-dichloro-5,6-dicyanobenzoquinone[8], have been studied. Also some studies are devoted to interaction of *p*-nitrophenol with free base meso-tetraphenylporphyrin. Uzan *et al.*[1] demonstrated that the interaction of *p*-nitrophenol with H_2TPP gives a 2 : 1 hydrogen-bonded complex in benzene and a 2 : 1 undissociative ion pair in dichloromethane. They showed that equilibrium could be shifted toward an ion pair when the dielectric constant of the medium increases.

The substituent X of free base porphyrin alters the electron density of the porphyrin ring. On the other hand, *p*-BrC_6H_4OH and *p*-ClC_6H_4OH have different tendencies toward complex formation with free base porphyrins. It seems that in *p*-BrC_6H_4OH and *p*-ClC_6H_4OH because of lower electron withdrawing properties of chlorine and bromine relative to nitro-group interactions with free base porphyrins are through formation of hydrogen bond complexes. It is expected, therefore, that the substituent effect on formation of molecular complex between free base porphyrins and phenols can be studied.

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In the present work, the thermodynamic parameters for the interaction of *p*-halophenols with *meso*-tetraphenylporphyrin (H_2TPP), *meso-tetrakis*-(4-chlorophenyl)porphyrin ($H_2T(4\text{-}Cl)PP$), *meso-tetrakis*-(3-chlorophenyl)porphyrin ($H_2T(3\text{-}Cl)PP$), *meso-tetrakis*-(4-methylphenyl)porphyrin ($H_2T(4\text{-}CH_3)P()$, *meso-tetrakis*-(3-methylphenyl)porphyrin ($H_2T(3\text{-}CH_3)PP$) and *meso-tetrakis*-(4-methoxyphenyl)porphyrin ($H_2T(4\text{-}CH_3O)PP$) in chloroform as a solvent.

EXPERIMENTAL

Benzaldehyde, *p*-substituted benzaldehydes, propionic acid, chloroform and *p*-halophenols (Merck and Fluka) were used as received. Pyrrole (Fluka) was distilled before use. Chloroform solvent for UV-Vis measurements was distilled over K_2CO_3 before use. H_2TPP, $H_2T(4\text{-}Cl)PP$, $H_2T(3\text{-}Cl)PP$, $H_2T(4\text{-}CH_3)PP$, $H_2T(3\text{-}CH_3)PP$, $H_2T(4\text{-}CH_3O)PP$ were prepared and purified by the usual methods[9].

UV-Vis measurements were performed using a Jasco V-530 UV-Vis spectrometer equipped with a LAUDA ecoline RE 104 thermostat. The measurements were carried out by a titration method at 5, 10, 15, 20 and 25°C in duplicated experiments. In a typical measurement, 2.5 mL solution of H_2TPP (2.5×10^{-6} M) in chloroform was titrated by *p*-ClC_6H_4OH (3 M). UV-Vis spectra were recorded over a range of 396–710 nm; about 10–15 wavelengths that have suitable variations of absorbance were selected, and the formation constants and the other thermodynamic parameters of adduct formation were calculated. The overall formation constants K (M^{-2}) were calculated by the SQUAD program[10, 11].

RESULTS AND DISCUSSION

Upon the addition of excess of *p*-halophenols to a solution of free base porphyrin in chloroform, its purple color changes to green. This change in color is due to the interactions of *p*-halophenol compounds with free base porphyrins. Interactions of *p*-halophenols with free base porphyrins were studied by means of UV-Vis spectrophotometry.

Thermodynamic studies: Upon the interaction of *p*-halophenols with free base tetraarylporphyrins the original peaks of tetraarylporphyrins slowly changed and two new peaks appeared (Fig. 1). For example, upon the titration of $H_2T(3\text{-}CH_3)PP$ with *p*-BrC_6H_4OH, the original peaks (418, 514, 548, 590 and 646 nm) changed and the new peaks appeared at 448 and 664 nm. The clear isosbestic points in Fig. 1 represent adduct formations in solution. Tables 1 and 2 give the original peaks of free base porphyrins and new peaks produced by the addition of *p*-halophenols to a solution of porphyrin in chloroform.

The thermodynamic parameters are useful tools for studying these interactions and understanding the relative stabilities of adducts. The overall formation constant K (M^{-2}) for 2 : 1 adducts, considering the previous studies[1], were determined at several temperatures by analyzing the concentration and the temperature dependence of UV-Vis absorption by a SQUAD program (Tables 3, 4). Van't Hoff plots of these overall formation constants, K (M^{-2}), lead to other thermodynamic parameters, H° and S° (Tables 5, 6).

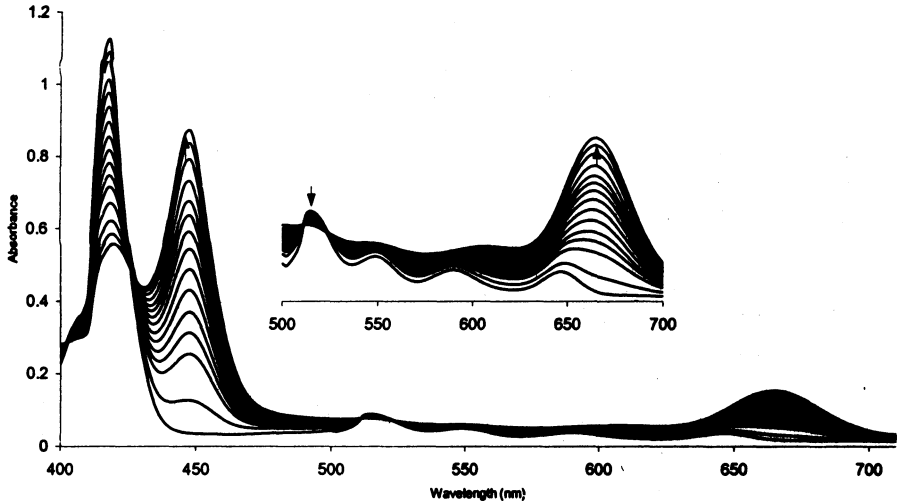

Fig. 1. Typical titration spectra for titration of $H_2T(3\text{-}CH_3)PP$ with *p*-BrC_6H_4OH in chloroform. Bands appearing at 448 and 664nm are related to adduct.

TABLE-1
UV-VIS BANDS λ($CHCl_3$/nm) OF THE FREE BASE PORPHYRINS AND THEIR ADDUCTS WITH *p*-ClC_6H_4OH

H_2TPP	417	514	549	589	646
H_2TPP (adduct)	442	—	—	—	660
$H_2T(3\text{-}Cl)PP$	418	514	550	590	646
$H_2T(3\text{-}Cl)PP$ (adduct)	448	—	—	—	674
$H_2T(3\text{-}CH_3)PP$	418	514	548	590	646
$H_2T(3\text{-}CH_3)PP$ (adduct)	446	—	—	—	662
$H_2T(4\text{-}CH_3)PP$	419	516	552	591	647
$H_2T(4\text{-}CH_3)PP$ (adduct)	446	—	—	—	674
$H_2T(4\text{-}CH_3O)PP$	420	518	555	593	650
$H_2T(4\text{-}CH_3O)PP$ (adduct)	454	—	—	—	694

$H_2T(4\text{-}Cl)PP$ shows no measurable interaction with *p*-halophenols under our experimental conditions. The data in Tables 3 and 4 show that the overall formation constant K (M^{-2}) of the adducts undergoes a regular increase from H_2TPP, $H_2T(4\text{-}CH_3)PP$, $H_2T(3\text{-}CH_3)PP$, $H_2T(3\text{-}Cl)PP$ to $H_2T(4\text{-}CH_3O)PP$. For example, at 20°C the following order of the overall formation constants, K (M^{-2}) have been observed:

$ClC_6H_4OH\text{-}H_2T(4\text{-}Cl)PP < ClC_6H_4OH\text{-}H_2TPP < ClC_6H_4OH\text{-}H_2T(4\text{-}CH_3)PP < ClC_6H_4OH\text{-}H_2T(3\text{-}CH_3)PP < ClC_6H_4OH\text{-}H_2T(3\text{-}Cl)PP < ClC_6H_4OH\text{-}H_2T(4\text{-}CH_3O)PP$

$- < 3.47 < 5.13 < 6.17 < 7.94 < 13.18$

$BrC_6H_4OH\text{-}H_2T(4\text{-}Cl)PP < BrC_6H_4OH\text{-}H_2TPP < BrC_6H_4OH\text{-}H_2T(4\text{-}CH_3)PP < BrC_6H_4OH\text{-}H_2T(3\text{-}CH_3)PP < BrC_6H_4OH\text{-}H_2T(3\text{-}Cl)PP < BrC_6H_4OH\text{-}H_2T(4\text{-}CH_3O)PP$

$- < 26.30 < 38.90 < 56.23 < 61.66 < 95.50$

TABLE-2
UV-VIS BANDS λ($CHCl_3$/nm) OF THE FREE BASE PORPHYRINS AND THEIR ADDUCTS WITH *p*-BrC_6H_4OH

H_2TPP	417	514	549	589	646
H_2TPP (adduct)	446	—	—	—	664
$H_2T(3\text{-Cl})PP$	418	514	550	590	646
$H_2T(3\text{-Cl})PP$ (adduct)	450	—	—	—	676
$H_2T(3\text{-}CH_3)PP$	418	514	548	590	646
$H_2T(3\text{-}CH_3)PP$ (adduct)	448	—	—	—	664
$H_2T(4\text{-}CH_3)PP$	419	516	552	591	647
$H_2T(4\text{-}CH_3)PP$ (adduct)	450	—	—	—	676
$H_2T(4\text{-}CH_3O)PP$	420	518	555	593	650
$H_2T(4\text{-}CH_3O)PP$ (adduct)	456	—	—	—	698

TABLE-3
THE FORMATION CONSTANTS LOG (K/M^{-2}) FOR ClC_6H_4OH-TETRAARYLPORPHYRIN SYSTEMS IN $CHCl_3$ SOLVENT

Temperature (°C)	5	10	15	20	25
$H_2T(4\text{-Cl})PP$	—	—	—	—	—
H_2TPP	0.24(±0.01)	0.35(±0.01)	—	0.54 (±0.05)	0.65(±0.02)
$H_2T(4\text{-}CH_3)PP$	0.33(±0.04)	0.54(±0.05)	—	0.71(±0.02)	0.85(±0.01)
$H_2T(3\text{-}CH_3)PP$	0.41(±0.03)	0.56(±0.02)	—	0.79(±0.02)	0.96(±0.02)
$H_2T(3\text{-Cl})PP$	0.50(±0.02)	0.66(±0.01)	—	0.90(±0.01)	1.05(±0.05)
$H_2T(4\text{-}CH_3O)PP$	0.53(±0.01)	0.72(±0.03)	0.96(±0.02)	1.12(±0.01)	—

TABLE-4
THE FORMATION CONSTANTS log (K/M^{-2}) FOR BrC_6H_4OH-TETRAARYLPORPHYRIN SYSTEMS IN $CHCl_3$ SOLVENT

Temperature (°C)	5	10	15	20	25
$H_2T(4\text{-Cl})PP$	—	—	—	—	
H_2TPP	1.09(±0.01)	—	1.28(±0.01)	1.42(±0.05)	1.49(±0.02)
$H_2T(4\text{-}CH_3)PP$	1.24(±0.02)	—	1.51(±0.01)	1.59(±0.01)	1.72(±0.05)
$H_2T(3\text{-}CH_3)PP$	1.35(±0.03)	1.53(±0.02)	1.61(±0.02)	1.75(±0.02)	—
$H_2T(3\text{-Cl})PP$	1.37(±0.04)	—	1.66(±0.05)	1.79(±0.02)	1.90(±0.01)
$H_2T(4\text{-}CH_3O)PP$	—	1.68(±0.01)	1.86(±0.03)	1.98(±0.02)	2.11(±0.01)

Comparison of these formation constants with the equilibrium constants of *p*-nitrophenol-tetraphenylporphyrin complexes reported by Uzan *et al.*[1], 113 M^{-2} in benzene and 6.46 ($K_1 = 3.4$, $K_2 = 1.9$) in dichloromethane shows a good agreement between these data.

Tables 5 and 6 show the thermodynamic parameters obtained for the interactions of *p*-halophenols with free base porphyrins in chloroform.

Our results show that the kind and position of substituent (X) on the phenyl rings of the free base porphyrin influences the interactions of the corresponding porphyrin with the *p*-halophenols. The free energy of adduct formation becomes more negative through the series H_2TPP, $H_2T(4\text{-}CH_3)PP$, $H_2T(3\text{-}CH_3)PP$, $H_2T(3\text{-}Cl)PP$ to $H_2T(4\text{-}CH_3O)PP$ which indicates the stronger interaction along this sequence.

TABLE-5
THE OVERALL THERMODYNAMIC PARAMETERS H°, S° and G° FOR ADDUCTS OF ClC_6H_4OH WITH FREE BASE PORPHYRINS IN $CHCl_3$[a]

	ΔH°	ΔS°	ΔG°
$H_2T(4\text{-}Cl)PP$	—	—	—
H_2TPP	32.1(1)	120.1(3)	–2.5(1)
$H_2T(4\text{-}CH_3)PP$	41.4(3)	154.5(12)	–2.7(3)
$H_2T(3\text{-}CH_3)PP$	41.7(2)	157.9(7)	–3.8(2)
$H_2T(3\text{-}Cl)PP$	42.6(2)	162.9(6)	–4.3(2)
$H_2T(4\text{-}CH_3O)PP$	62.3(3)	234.7(9)	–5.3(3)

[a] H° (kJ mol^{-1}), S° (J K^{-1} mol^{-1}) and G° (kJ mol^{-1}) at 15°C

TABLE-6
THE OVERALL THERMODYNAMIC PARAMETERS H°, S° AND G° FOR ADDUCTS OF BrC_6H_4OH WITH FREE BASE PORPHYRINS IN $CHCl_3$a

	ΔH°	ΔS°	ΔG°
$H_2T(4\text{-}Cl)PP$	—	—	—
H_2TPP	32.9(±2)	138.9(±7)	–7.1(±2)
$H_2T(4\text{-}CH_3)PP$	38.0(±2)	162.8(±7)	–8.8(±2)
$H_2T(3\text{-}CH_3)PP$	40.4(±3)	171.4(±12)	–9.0(±3)
$H_2T(3\text{-}Cl)PP$	41.9(±2)	176.2 (±7)	–8.9(±2)
$H_2T(4\text{-}CH_3O)PP$	45.6(±2)	193.6(±8)	–10.2(±2)

[a] H° (kJ mol^{-1}), S° (J K^{-1} mol^{-1}) and G° (kJ mol^{-1}) at 15°C.

On the other hand, the stability of molecular complexes for a certain free base depends on the type of halide substituent on the phenol; BrC_6H_4OH forms more stable adducts than ClC_6H_4OH. From inductive electron withdrawing and resonance electron releasing properties of chlorine atom of *p*-ClC_6H_4OH, which operate in opposite directions, the resonance electron releasing effects are more important, therefore, causes a reduction in the tendency of *p*-ClC_6H_4OH to form hydrogen-bonding complexes with free base porphyrins. But in *p*-BrC_6H_4OH, because of bulkiness, the bromine atom shows no considerable resonance electron donating interaction with the phenyl ring, therefore, inductive electron withdrawing effect is more important and it has a greater tendency to formation of hydrogen-bond molecular complexes with the free base porphyrins. In all, the inductive electron withdrawing effects are more effective than the resonance electron releasing effects in the formation of hydrogen-bond molecular complexes.

Primarily, the formation of a 1 : 1 molecular complex is expected. This 1 : 1 complex induces a distortion in the porphyrin plane; this deformation would enhance the interaction ability of porphyrin macrocycle. Therefore, the distorted porphyrins more readily accept a second phenol molecule at the opposite side and favour the formation of a 2 : 1 adduct. The adducts have positive values of H°, S°. A greater contribution of S° relative to H° leads to a negative value of G° in the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The positive change of S° returns to an association between the *p*-halophenol and the free base porphyrin molecule, which is accompanied with releasing a large number of chloroform molecules that solvate the *p*-halophenol and the free base porphyrin (Tables 5 and 6). Our results show that in this range of temperature the interaction of the *p*-halophenols with the free base porphyrins is endothermic.

Also greater magnitude of binding constants, K, for the *m*- relative to the *p*-substituted porphyrins are probably due to a more distorted structure of *m*- free bases than the corresponding *p*- isomers that increase their hydrogen-bond formation abilities toward the *p*-halophenols. It seems that this distortion depends on the weight of the substituent, so that the weightier chlorine group leads to a more deformation in porphyrin structure with a greater tendency to formation of hydrogen-bond complex.

These results show that the interactions of the substituted free base tetraphenylporphyrins toward *p*-halophenol vary in the order:

$$H_2T(4\text{-}CH_3O)PP > H_2T(3\text{-}Cl)PP > H_2T(3\text{-}CH_3)PP > H_2T(4\text{-}CH_3)PP > H_2TPP > H_2T(4\text{-}Cl)PP$$

On the other hand, a comparison of the formation constants shows that *p*-BrC_6H_4OH has a stronger interaction with the free base porphyrins than *p*-ClC_6H_4OH.

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