Notes

Substituent Effects on Enthalpy and Entropy for the Axial Ligation of Zinc Tetraphenylporphyrinates

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Thermodynamic data were determined for the axial ligation of zinc tetra(substituted phenyl)porphyrinates by 1-methylimidazole in toluene. The data are used to (1) verify the isoequilibrium condition for the reaction and (2) determine the effect of the substituent on the enthalpy and entropy of reaction. Among *para*-substituted derivatives, the enthalpy exhibits no observable trend as the electron-donating–withdrawing ability of the substituents is varied. Relatively large entropy losses are associated with the presence of electron-donating *para* substituents.

The effect of substituents on the size of the equilibrium constants for the ligation of metalloporphyrins has been studied for a wide range of metals and Lewis bases. The axial ligation of 5,10,15,20-tetra(substituted phenyl)porphyrinate complexes of Zn,[1–3] Co,[4] VO,[5] Fe^{II},[6] Fe^{III},[7,8] and Ni[3] by amines has been found to follow the Hammett relationship (1) for *para*

$$\log K_X = \log K_H + 4\sigma\rho \qquad (1)$$

substituents X in various solvents. Here K_H and K_X are the equilibrium constants for the reaction of the unsubstituted (tpp) and substituted tetraphenylporphyrinate complexes, respectively, σ is the substituent constant, which reflects the electron-donating or -releasing character of X, and ρ reflects the sensitivity of the reaction to the electronic effect of the substituent. With the exception of $[Fe(tpp)]^+$ in $CHCl_3$, positive ρ values have been obtained for these reactions, indicating that axial ligation is favoured by electron-withdrawing substituents. In none of these studies has the variation of the standard enthalpy, ΔH°, and entropy, ΔS° with substituent been examined even though these effects are important to an understanding of the free-energy change. The lack of enthalpy and entropy data in previous studies also brings up the question of the validity of the extensive Hammett correlations which have been applied to these systems. In making these correlations it is assumed that the series of reactions exhibits an isoequilibrium condition and that the reaction is being studied at a temperature distant from the isoequilibrium temperature.[9] For large ρ values, the assumption is probably good. However, for small ρ values there exists the possibility that data were obtained too close to the isoequilibrium temperature, where the free-energy change will be constant regardless of substitution and the ρ value will be zero. In studying the variation in enthalpy and entropy with substituents for the axial ligation of [Zn(tpp)] we have verified the isoequilibrium condition for this reaction and determined the isoequilibrium temperature.

Experimental

Toluene was distilled from sodium metal and benzophenone and stored over molecular sieves prior to use. 1-Methylimidazole (mim) was vacuum distilled from calcium hydride and stored over molecular sieves.

The unsubstituted porphyrin, H_2tpp (5,10,15,20-tetraphenylporphyrin), the tetra(*ortho*- and *para*-substituted phenyl) derivatives (X = CF_3, Cl, CH_3, OCH_3 or NEt_2), and their corresponding zinc complexes were synthesised by the method of Adler *et al.*[10,11] Purification of the *o*-methoxy derivative was carried out as described previously.[1] The remaining zinc porphyrins were purified by chromatography on dry alumina in $CHCl_3$, dried at 100–120 °C, and then stored at 0 °C until used. The porphyrins where X = *o*-Me or *o*-Cl were synthesised following Lindsey's method[12] for the preparation of tetramesitylporphyrin. Zinc(II) was inserted into the porphyrins by the method of Adler.[11]

Spectra were recorded on a Perkin-Elmer (PE) Lambda 4 ultraviolet–visible spectrophotometer with sample temperatures regulated by a PE temperature controller. Absorbance data were obtained for the reaction of the zinc porphyrins with 1-methylimidazole at 20.0, 25.0, 30.0 and 35.0 (±0.1 °C) as described below. A fixed aliquot of the metalloporphyrin and variable amounts of mim in toluene were mixed and diluted to 2.5 cm^3, giving a series of solutions with constant metalloporphyrin concentration and varying base concentrations. The absorbances of the solutions at 550 nm were monitored as a function of base concentration.

Equilibrium constants were determined by the method of Miller and Dorough as described previously.[13] Enthalpies and entropies of reaction and their standard deviations were determined from a least-squares fit of the temperature dependence of ln K using the program GRAFIT[14] (Sigma Chemical Co.).

Results and Discussion

1-Methylimidazole reacts with [Zn(tpp)] and derivatives to produce a 1:1 adduct in which mim is co-ordinated to the zinc atom along an axial axis. Table 1 contains equilibrium constants, enthalpies, and entropies for the reaction of the tetra(substituted phenyl)porphyrinate complexes with mim. The substituents employed (X) were X = H, *p*-CF_3, *o*- or *p*-Cl, -Me, -OMe and *p*-NEt_2. In all cases, a spectral titration of the zinc porphyrin with mim revealed isosbestic points between 350 and 750 nm, indicating the presence of only two absorbing species in solution, the uncomplexed zinc porphyrin and the 1:1 adduct.

Hammett Correlation.—The equilibrium constants determined at 25 °C were used for fitting by the classical Hammett equation (1). A list of *para* sigma constants used in this work can be found in ref. 13. *ortho*-Substituent constants were obtained

Table 1 Thermodynamic data for the reactions of zinc tetra(substituted phenyl)porphyrinates with 1-methylimidazole; standard deviations are given in parentheses

Substituent	K/dm^3 mol^{-1} (298 K)	$-\Delta H$/kJ mol^{-1}	$-\Delta S$/J K^{-1} mol^{-1}
o-Cl	2.21 (0.09) × 10^5	45.8 (2.0)	51.4 (6.8)
H	5.41 (0.12) × 10^4	42.9 (1.4)	53.1 (4.5)
o-Me	5.28 (0.06) × 10^4	53.2 (2.1)	88.0 (7.0)
o-OMe	8.28 (0.20) × 10^3	41.1 (0.8)	63.1 (2.6)
p-CF_3	2.44 (0.12) × 10^5	47.6 (1.4)	56.1 (4.5)
p-Cl	1.61 (0.08) × 10^5	49.1 (1.0)	65.3 (3.3)
p-Me	4.95 (0.16) × 10^4	51.1 (0.7)	81.7 (2.2)
p-OMe	4.48 (0.11) × 10^4	52.3 (1.4)	86.4 (4.7)
p-NEt_2	1.79 (0.06) × 10^4	48.7 (1.3)	82.2 (4.4)

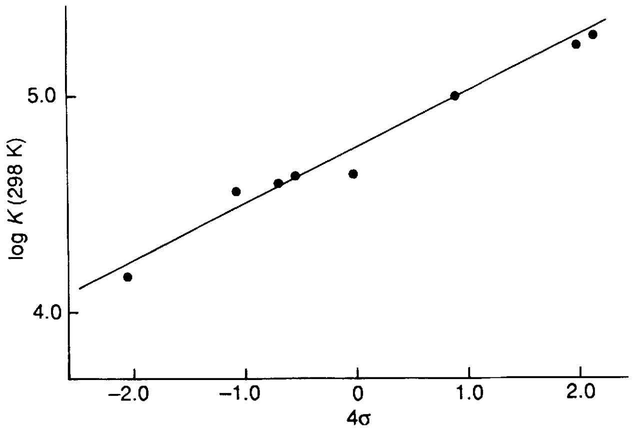

Fig. 1 Hammett plot for the reaction of zinc tetra(substituted phenyl)porphyrinates with 1-methylimidazole at 298 K. The point for X = *o*-OMe has been deleted

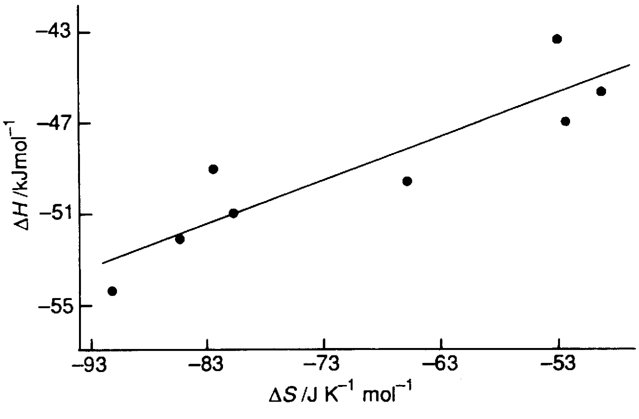

Fig. 2 Plot of ΔH° *vs.* ΔS° for the reactions in Fig. 1

from the results of Tribble and Traynham.[15] A plot of log K for the *ortho*- and *para*-substituted phenylporphyrinate complexes *versus* 4σ is shown in Fig. 1. There is a good correlation ($r = 0.98$) between 4σ and log K for all data points except that for the *o*-methoxy substituent, which exhibits an equilibrium constant lower than that predicted by 4σ. A slope of 0.263 ± 0.021 was obtained from a least-squares fit of the data excluding the *o*-methoxy point. This value can be compared to values obtained for the reaction of zinc tetra(*para*-substituted phenyl)porphyrinates with other amines, 0.188 and 0.180 for the reaction with pyridine in benzene[2] and with 3-methylpyridine in toluene,[3] respectively and 0.208[12] for the reaction of [Zn(tpp)] with a copper(II) chelate containing an imidazolate moiety.

Enthalpy and Entropy Effects.—A criticism of Hammett correlations for reactions of zinc tetraphenylporphyrinates and similar systems reported in the literature is the lack of thermodynamic data supporting the applicability of the Hammett equation to the axial ligation of metalloporphyrins. This would not be a serious criticism except for the small values of ρ which have been reported. At the isoequilibrium temperature for a reaction the value of ρ should be zero, and therefore data obtained near the isoequilibrium temperature exhibit a decreased sensitivity toward substituent effects. Consequently, a value of ρ between 1 and −1 which has been obtained for data collected at a single temperature may be misleading since it is not possible to distinguish between a small ρ which implies a weak dependence of the reaction on substituent effects or one which arises because data is being collected at a temperature which is too close to the isoequilibrium temperature.[9] For this work, ΔH° and ΔS° were determined for the reaction of each substituted zinc porphyrinate with mim and a correlation of ΔH° with ΔS° was made. Data for the *o*-methoxy substituent were excluded since the corresponding complex did not fit the Hammett correlation. The correlation for the remaining eight complexes is shown in Fig. 2. A reasonable correlation ($r = 0.91$) is obtained. This is consistent with the requirement that in order for the Hammett relationship to be valid an isoequilibrium condition must exist, *i.e.* the change in ΔH° for the series of substituted complexes must be proportional to the change in ΔS°. From the slope of the plot, an isoequilibrium temperature of 176 ± 15 K is obtained which is well below the temperature range employed in this study.

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