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THERMODYNAMICS OF AXIAL COORDINATION REACTION OF *PARA*-SUBSTITUTED TETRAPHENYLPORPHINATOIRON(III) CHLORIDE

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ABSTRACT

The thermodynamics of axial coordination reactions of *para*-substituted tetraphenylporphinatoiron(III) chloride, (p-X)TPPFeCl, with various ligands (L = Im (imidazole), MeIm (2-methylimidazole), EMIm (2-ethyl-4-methylimidazole) in dichloromethane solvent have been studied.

$$(p-\mathrm{X})\mathrm{TPPFeCl} + n\mathrm{L} \overset{K_e}{=} [(p-\mathrm{X})\mathrm{TPPFeL}_n]^+\mathrm{Cl}^-$$

The steric and electronic effects of the three axial ligands are compared, and the effect of *para*-substituents on the phenyl rings is also discussed. Some linear relationships can be derived theoretically if Hammett relationships, isokinetic and isoequilibrium relationships show up in the system of similar reactions. These linear relationships have been verified by our experiments.

INTRODUCTION

Because of their biological importance, the reactions of iron porphyrins with imidazole, substituted (including N-substituted) imidazoles, etc., have been the subject of numerous thermodynamic studies [1–3]. We have studied the thermodynamics of axial coordination reactions of *para*-substituted tetraphenylporphinatoiron(III) chloride, (p-X)TPPFeCl (X = Cl, H, CH_3, CH_3O) with various ligands (L–Im (imidazole), MeIm (2-methylimidazole), EMIm (2-ethyl-4-methylimidazole)) in dichloromethane.

$$(p\text{-X})\mathrm{TPPFeCl} + n\mathrm{L} \overset{K_e}{=} [(p\text{-X})\mathrm{TPPFeL}_n]^+\mathrm{Cl}^- \qquad (1)$$

The equilibrium constant K_e and stoichiometric number of axial ligands n have been determined. The steric and electronic effects of three axial ligands have been compared, and are shown to affect the course of reaction (1). It

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has been found that Hammett relationships, isoequilibrium relationships, and some other linear relationships exist in the systems studied.

EXPERIMENTAL

Materials

(p-X)TPP and (p-X)TPPFeCl were synthesized by literature methods [4,5]. Satisfactory elemental analyses (C, H, N) were obtained for these compounds. Im and MeIm were recrystallized twice from absolute alcohol and dried in vacuo; EMIm was of analytical reagent grade. The solvent dichloromethane (analytical grade) was further treated by a literature method [6] before use.

Method of measurement

The equilibrium constant K_e and the stoichiometric number of axial ligands (n) in reaction (1) were determined by a spectrophotometric titration method at 510 nm. Spectrophotometric measurements were made in dichloromethane on a Beckman DU-8B spectrophotometer. The experimental data were treated with an Apple II microcomputer by applying eqn. (2). Since the axial ligands have no absorption in the chosen wavelength range, eqn. (2)

$$\ln\left(\frac{A_e - A_0}{A_\infty - A_e}\right) = n \ln C_L + \ln K_e \tag{2}$$

may be rearranged to give eqn. (3) in the presence of a large excess of ligands

$$\frac{A_0}{A_e - A_0} = \frac{\epsilon_1}{\epsilon_2 - \epsilon_1} \cdot \frac{1}{K_e C_L^n} + \frac{\epsilon_1}{\epsilon_2 - \epsilon_1} \tag{3}$$

where A_0 is the absorbance of (p-X)TPPFeCl in the absence of ligand, A_e is the absorbance of the equilibrium system in the presence of a large excess of ligands, and ϵ_1 and ϵ_2 are the extinction coefficients of the reactants and products, respectively. As long as the stoichiometric number n was determined, $A_0/(A_e - A_0)$ was linearly correlated with $1/C_L^n$ to evaluate K_e. In this way, the difficulty of measuring A_∞ could be overcome.

RESULTS AND DISCUSSION

Effect of different axial ligands

The stoichiometric number of axial ligands (n) and equilibrium constant (K_e) determined according to eqns. (2) and (3) are given in Table 1. It can

TABLE 1

Stoichiometric number and equilibrium constant of different ligands reacting with (p-Cl)TPPFeCl at 20 ° C

L	Im	MeIm	EMIm
n	2.02	1.97	0.996
K_e	9.72×10^5	4.18×10^4	48.76
r	0.999	0.994	0.999

r = correlation coefficient.

be seen that the sequence of magnitude of equilibrium constants is as follows: $K_e(\text{Im}) > K_e(\text{MeIm}) > K_e(\text{EMIm})$. The order of nucleophilic power of the ligands is Im < MeIm < EMIm, which means that K_e(EMIm) should be the largest, whereas the order of steric inhibition effect of the ligands is Im < MeIm < EMIm, which means that K_e(Im) would be the largest. According to the experimental data, the steric effect predominates over the electronic effect. Therefore, the larger the steric inhibition effect, the smaller is the equilibrium constant. Furthermore, the steric inhibition of EMIm is so large that a second EMIm ligand can not approach the central iron ion. Thus the stoichiometric number n of ligand EMIm is unity.

Effect of para-substituents in the phenyl rings

The equilibrium constants of reaction (1) (L ≡ Im) at different temperatures are shown in Table 2; so, too, are the standard change of molar enthalpy $\Delta H_m^\ominus$ and the standard change of molar entropy $\Delta S_m^\ominus$ of these reactions. The order of the K_e, $\Delta H_m^\ominus$ and $\Delta S_m^\ominus$ values is as follows: $K_e(\text{OCH}_3) < K_e(\text{CH}_3) < K_e(\text{H}) < K_e(\text{Cl})$; $|\Delta H_m^\ominus(\text{OCH}_3)| < |\Delta H_m^\ominus(\text{CH}_3)| < |\Delta H_m^\ominus(\text{H})| < |\Delta H_m^\ominus(\text{Cl})|$; $|\Delta S_m^\ominus(\text{OCH}_3)| < |\Delta S_m^\ominus(\text{CH}_3)| < |\Delta S_m^\ominus(\text{H})| < |\Delta S_m^\ominus(\text{Cl})|$. Since the central iron ion is electrophilic, the electron-donating substituent on the phenyl rings should increase the electron density of the central nitrogen atoms of porphyrin and

TABLE 2

Equilibrium constants (K_e), standard change of molar enthalpy $\Delta H_m^\ominus$ and standard change of molar entropy $\Delta S_m^\ominus$ of reaction (1)

	$K_e/(10^5\ \text{mol}^{-2}\ \text{dm}^6)$				$-\Delta H_m^\ominus$ (kJ mol^{-1})	$-\Delta S_m^\ominus$ (J mol^{-1} K^{-1})	r [a]
	15 ° C	20 ° C	25 ° C	30 ° C			
p-Cl	18.7	9.72	4.84	2.66	95.1	210	0.9993
H	20.8	11.0	6.30	3.31	88.2	185	0.9995
p-CH$_3$	21.2	11.8	7.06	4.08	79.3	154	0.9999
p-OCH$_3$	22.2	12.7	7.92	4.63	75.2	139	0.9996

[a] r is the correlation coefficient of ln K_e vs. $1/T$.

make the product $[(p\text{-X})\text{TPPFeIm}_2]^+\text{Cl}^-$ more stable. Therefore, the stronger the electron-donating ability of the substituent, the larger is the equilibrium constant. Both Mössbauer and ESR spectra [7] showed that the reactant (p-X)TPPFeCl is a five coordinated complex of high spin ($s = 5/2$) and the product $[(p\text{-X})\text{TPPFeIm}_2]^+\text{Cl}^-$ is six coordinated and of low spin ($s = 1/2$). The two electrons at the high energy level are transmitted to the low energy level, accompanying the axial coordination reaction. This is therefore an exothermic process and $\Delta H_m^\ominus$ has a negative value. The electron-donating substituent degrades the interval between energy levels to diminish the energy released in the axial coordination reaction. Reaction (1) is a degrading process of the species numbers, and $\Delta S_m^\ominus$ is therefore negative. This means that, the stronger the electron-donating ability of the substituents, the smaller are the $|\Delta H_m^\ominus|$ and $|\Delta S_m^\ominus|$ values.

Isoequilibrium relationships (compensational effect)

Leffler [8] showed that the isoequilibrium relationships (4) and the isokinetic relationships (5) might exist in some system of similar reactions.

$$\Delta H_m^\ominus = \Delta H_0^\ominus + \beta\,\Delta S_m^\ominus \tag{4}$$

$$\Delta^{\neq} H_m = \Delta^{\neq} H_0 + \beta\,\Delta^{\neq} S_m \tag{5}$$

where β is the isoequilibrium temperature in eqn. (4) or isokinetic temperature in eqn. (5). A plot of $\Delta H_m^\ominus$ vs. the $\Delta S_m^\ominus$ values in Table 2 gives a straight line, with $\Delta H_0^\ominus$ as the intercept, which may be expressed by the following regression equation

$$\Delta H_m^\ominus = -36.06 + 281.4\,\Delta S_m^\ominus \qquad r = 0.9999$$

The high correlation coefficient indicates the existence of an isoequilibrium relationship in the system. The isoequilibrium temperature β was found to be 281. 4 K in our case. Similarly, the kinetic measurement [7] of reaction (1) with ligand Im gave the following result.

$$\Delta^{\neq} H_m = 49.89 + 262.7\,\Delta^{\neq} S_m \qquad r = 0.9994$$

and the isokinetic temperature β was found to be 262.7 K.

Linear free energy relationships

Our experimental results showed that Hammett linear relationships (6) [9] existed in the system studied.

$$\ln[K_e(\text{X})/K_e(\text{H})] = \rho_T(4\sigma_\text{x}) \tag{6}$$

Since there are four phenyl substituents on one porphyrin ring, the Hammett substituent constant may be expressed as $4\sigma_\text{x}$. When $\ln K_e(\text{X})$ in Table 2 was linearly regressed against $4\sigma_x$ at different temperatures, the following linear equations were obtained

15°C $\ln K_e(\mathrm{X}) = -0.08011(4\sigma_x) + 14.53 \qquad r = 0.970$

20°C $\ln K_e(\mathrm{X}) = -0.1303(4\sigma_x) + 13.91 \qquad r = 0.997$

25°C $\ln K_e(\mathrm{X}) = -0.2395(4\sigma_x) + 13.32 \qquad r = 0.995$

30°C $\ln K_e(\mathrm{X}) = -0.2772(4\sigma_x) + 12.73 \qquad r = 0.997$

The Hammett ρ_T values were negative for the system studied, providing further evidence to show that electron-donating groups favour the axial coordination reaction. According to the literature [10], eqn. (7) could be derived theoretically if eqns. (4) and (6) are applied to the system studied.

$$\rho_T = \rho_\infty(1 - \beta/T) \tag{7}$$

where the Hammett parameter ρ_∞ is a constant which equals ρ_{T} as the temperature tends to ∞. In the system studied the following equation was found

$$\rho_T = -4.322\,(1 - 283.0/T) \qquad r = 0.98$$

Thus $\rho_\infty = -4.322$ and $\beta = 283.0$ K.

Let δ_{X} represent the related value operator of substituent X, e.g. $\delta_{\mathrm{X}} f = f(\mathrm{X}) - f(\mathrm{H})$. Substituting eqn. (4) into $\Delta G_m^\ominus = \Delta H_m^\ominus - T\,\Delta S_m^\ominus$ gives

$$\Delta G_m^\ominus = \Delta H_0^\ominus + (\beta - T)\,\Delta S_m^\ominus \tag{8}$$

therefore

$$\delta_x\,\Delta G_m^\ominus = (\beta - T)\delta_x\,\Delta S_m^\ominus \tag{9}$$

Substituting $\Delta G_{\mathrm{m}}^\ominus = -RT \ln K_e$ into (6) yields

$$\delta_x\,\Delta G_m^\ominus = -RT \ln[K_e(\mathrm{X})/K_e(\mathrm{H})] = -RT\rho_T(4\sigma_x) \tag{10}$$

According to eqns. (7), (9), and (10) it can be derived that

$$\delta_x\,\Delta S_m^\ominus = R\rho_\infty(4\sigma_x) \tag{11}$$

$$\delta_x\,\Delta H_m^\ominus = \beta\delta_x\,\Delta S_m^\ominus = \beta R\rho_\infty(4\sigma_x) \tag{12}$$

In the system studied the following equations were found

$$\Delta H_m^\ominus(\mathrm{X}) = -10130(4\sigma_x) - 86580 \qquad r = 0.992$$

$$\Delta S_m^\ominus(\mathrm{X}) = -36.04(4\sigma_x) - 179.6 \qquad r = 0.993$$

However, the values $\rho_\infty = -4.334$ and $\rho = 281.1$ K are obtained from eqs. (11) and (12).

It is seen that the values β and ρ_∞ obtained by different approaches in the system studied agree pretty well, which not only means that these linear relationships exist in the system, but also proves our derivations and data treatment to be correct.

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