Thermodynamic Study of the Substitution Reaction between *Cis*-[Pt(*p*-MeC₆H₄)₂(SMe₂)₂] Complex and pyridine-3-ol Ligand

*ALIREZA AKBARI, MEHDI AHMADI AND BABAK GOLZADEH

Chemistry Department, Payame Noor University, 19395-4697 Tehran, I. R. of IRAN
a_akbari@pnu.ac.ir

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Abstract: The equilibrium constants and other thermodynamic parameters for the adduct formation between *cis*-[Pt(*p*-Tol)₂(SMe₂)₂] complex as an acceptor and 3-hydroxy pyridine (pyridine-3-ol) ligand as a donor in acetone, ethanol and benzene at various temperatures (13-20°C) have been spectrophotometrically measured. Our studies showed that ΔH° (KJ.mol⁻¹) of the reaction in ethanol, acetone and benzene are 6.442, 43.1 and 46.247 respectively. The related entropies (J.mol⁻¹.K⁻¹) have been obtained 89.82, 218.5 and 236 respectively, too. In addition, the amount of ΔG° (kJ.mol⁻¹) for the reaction occurred in solvents mentioned above are -20.324, -22.013 and -24.081.

Keywords: platinum; complex; thermodynamic; equilibrium constant; enthalpy; entropy; Gibb's energy.

Introduction

Platinum complexes are now among the most widely used drugs for the treatment of cancers [1,2]. Among them, *cis*-platin is one of the effective antitumor agents used to treat various types of human cancers [3,4]. In this view, ligand substitution reactions on monomeric square planar platinum(II) complexes have been extensively studied [5]. During the past two decades, there has been a great interest in ligand substitution reactions of organoplatinum(II) complexes containing one or more Pt-C bonds [6-10].

Commonly, ligand exchange has been recognized as the initial step of many fundamental processes involving square-planar organometallic complexes [11]. So many related studies could be found in areas such as thermal decomposition of alkyl compounds [12-14], insertion of olefins into the M-H bond [15], oxidative addition and reductive elimination reactions [16], geometrical isomerization [17], electrophilic attack at the metal-carbon bond [18], exchange reactions [19] and the fluxionary motions of coordinated ligands [20]. These

mentioned fields of study might be considered from thermodynamic and kinetic aspects of chemical reactivity of platinum or other metal complexes [21-22].

In the present study, we describe the thermodynamics of *cis*-[Pt(*p*-Tol)₂(3-hydroxy pyridine)₂] complex formation, starting by *cis*-[Pt(*p*-Tol)₂(SMe₂)₂] precursor, and due to the donating characteristics of solvents, we then obtain the thermodynamic parameters for the ligand exchange and substitution process of this reaction in some solvents.

Experimental

The compounds 3-hydroxy pyridine, acetone, ethanol, benzene was of analytical grade. *Cis*-[Pt(*p*-Tol)₂(SMe₂)₂] complex was prepared with a previously reported method [23]. For this purpose, in a typical experiment a freshly prepared solution of *p*-tolyl lithium (4 ml) was added slowly to a stirred, ice-cooled solution of finely powdered [PtCl₂(SMe₂)₂] (200 mg; 0.5 mmol) in dry ether (10 ml). The reaction mixture was stirred for 2 h at 0°C and subsequently hydrolyzed with a few milliliters of saturated solution of NH₄Cl in water. Separation of the organic layer, extraction with ether, drying over MgSO₄ and evaporation gave a mixture of *cis*-[Pt(*p*-Tol)₂(SMe₂)₂] and [Pt₂(*p*-Tol)₄(μ-SMe₂)₂]. The off white residue was treated with SMe₂ (1mL) in CH₂Cl₂ (20 ml) in order to convert the coexisted dimeric species into the monomer. The solvent was evaporated and the residue was washed with a few milliliters of acetone. The reaction yield was 74% with a melting point of 88°C (d). The product was identified with its ¹H NMR spectrum and used as initial complex in this study.

Instrumental

Thermodynamic studies were carried out by a Shimadzu-2550 spectrophotometer with temperature control using an Index Instrument GD120 constant-temperature bath.

Method

3ml of initial complex (2×10⁻⁴ mol L⁻¹ in ethanol) containing a little SMe₂ due to prevent dimerization in solution, was transferred into the thermostatic cell compartment of the UV-Vis spectrophotometer, which was kept at a constant temperature by circulating water. Then, the ligand (0.05 mol L⁻¹ in ethanol) was added stepwise as it is common in the regular thermodynamic studies. Finally, the K_{eq} values were extracted using the fitting of obtained data.

Results and Discussion

Thermodynamic Studies

The complex was obtained from the reaction shown in equations 1 in which X, Y and Z are the initial complex, the ligand and the product complex respectively.

The absorption measurements were carried out in the range of 330-360 nm after the equilibrium was achieved. In this range, the ligand shows no absorption. The equilibrium constants and molar absorption of the complex were determined by measuring the absorbance in various concentrations of 3-hydroxy pyridine and constant *cis*-[Pt(*p*-Tol)₂(SMe₂)₂] concentration by non-linear curve fitting using KaleidaGraph program [24]. When 3-hydroxy pyridine as a donor (D) reacts with *cis*-[Pt(*p*-Tol)₂(SMe₂)₂] ions as an acceptor (A) to form the new complex, then K_{eq} for the equation 1 is:

$$K_{eq} = \frac{[Z]_{eq}}{[X]_{eq}[Y]_{eq}} \quad (2)$$

The observed absorbance of the solution is:

$$A = \varepsilon_{oX}[X]_{eq} + \varepsilon_{oY}[Y]_{eq} + \varepsilon_{oZ}[Z]_{eq} \quad (3)$$

The donor shows no absorption in the range of 330 to 360 nm. Thus, the above equation will be summarized as below:

$$A = \varepsilon_{oX}[X]_{eq} + \varepsilon_{oZ}[Z]_{eq} \quad (4)$$

Besides, the initial concentration of X is obtained by the Eq. 5:

$$[X]_o = [X]_{eq} + [Z]_{eq} \quad (5)$$

As a result, the product concentration in equilibrium time will be obtained by the following equations:

$$[Z]_{eq} = [X]_o - [X]_{eq} = K_{eq}[X]_{eq}[Y]_{eq} \quad (6)$$

and:

$$[X]_{eq} = \frac{[X]_o}{1 + K_{eq}[Y]_{eq}} \quad (7)$$

and:

$$[Z]_{eq} = \frac{K_{eq}[X]_o[Y]_{eq}}{1 + K_{eq}[Y]_{eq}} \quad (8)$$

Substituting $[X]_{eq}$ and $[Z]_{eq}$ into Eq. 5, then we obtain the following result:

$$A = \frac{\varepsilon_{oX}[X]_o + \varepsilon_{oZ}K_{eq}[X]_o[Y]_{eq}}{1 + K_{eq}[Y]_{eq}} \quad (9)$$

where ϵ is the molar absorption of the species denoted.

Figure 1 shows the increase in absorption bands in the range of 330-360 nm for the reaction between $\text{cis-[Pt(p-Tol)}_2(\text{SMe}_2)_2]$ and $\text{C}_5\text{H}_5\text{NO}$ at various additions of ligand in $\text{C}_2\text{H}_5\text{OH}$ at 13°C .

Figure 1. Electronic spectra variation of the reaction between $\text{cis-[Pt(p-Tol)}_2(\text{SMe}_2)_2]$ and $\text{C}_5\text{H}_5\text{NO}$ in $\text{C}_2\text{H}_5\text{OH}$ at $T=13^\circ\text{C}$ (molarities of entering ligand varied).

As it is shown, increase in the absorption was carried out after the first addition of new ligand, and the absorption was moderately constant after a while. If the reaction is completed, it is no need to add more ligand. If not, more addition of ligand is necessary because there is an equilibrium state between reactants and product. While the new ligand is added in separate steps, the absorption increases and moderately gets constant after a while again, i.e. there is an equilibrium between reactants and product, and finally, the reaction is almost completed because there is no obvious change in absorption after the last addition of ligand. If we select just the final spectrum of each addition and collect the absorption in the selected wavelength, 330nm, we can draw the plot of absorptions vs. molarities of the ligand as shown in Figure 2. The m_1 , m_2 , and m_3 values show ϵ_{OX} , ϵ_{OZ} , and K_{eq} respectively based on the curve fit definition in KaleidaGraph program.

Figure 2. The plot of Abs vs. molarities of the ligand for $cis-[Pt(p-Tol)_2(SMe_2)_2]$ reaction with C_5H_5NO at $T=13\text{ }^\circ C$ in C_2H_5OH .

Figure 3 demonstrates the plots of absorption vs. molarities of the ligand for the reaction between $cis-[Pt(p-Tol)_2(SMe_2)_2]$ and C_5H_5NO at various temperatures in C_2H_5OH . The equilibrium constants, K_{eq} , for this reaction at 13, 15, 17 and $20^\circ C$ are obtained as 3257.6 ± 612.4 , 3352.1 ± 396.24 , 3433.1 ± 486.34 , and 3475.6 ± 606.02 respectively.

Figure 3. The plots of Abs vs. molarities of the ligand for $cis-[Pt(p-Tol)_2(SMe_2)_2]$ reaction with C_5H_5NO at various temperatures in C_2H_5OH .

The same is valid for other systems, as well. The equilibrium constants of the studied *cis*-[Pt(*p*-Tol)₂(C₅H₅NO)₂] complex in three various solvents are shown in table 1.

Table 1. Equilibrium constant for *cis*-[Pt(*p*-Tol)₂(SMe₂)₂] with various C₅H₅NO at different temperatures in acetone, ethanol and benzene.

T°C	13°C	15°C	17°C	20°C
K _{eq} in ethanol	3257.5	3352.1	3433.1	3475.6
K _{eq} in acetone	3475.6	3964.6	4542.2	5350.1
K _{eq} in benzene	7227.7	8864.5	10115	11745

K_{eq} = equilibrium constant.

Thermodynamic parameters

The thermodynamic parameters of the studied reaction of platinum(II) complex were calculated by the van't Hoff equation ,10:

$$\ln K_{eq} = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (10)$$

in which K_{eq} and R are the equilibrium and gas constants respectively, and T is the temperature in the Kelvin scale. The values of ΔH° and ΔS° were obtained as 6441.69 J.mol⁻¹, 89.82 J.mol⁻¹.K⁻¹ from the slope and the intercept of the related linear plot (lnK_f vs. 1/T) respectively as shown in Figure 4. Furthermore, the ΔG° of the reaction is calculated as -20.32 kJ.mol⁻¹ in ethanol.

Figure 4. The plot of LnK_{eq} vs. 1/T for *cis*-[Pt(*p*-Tol)₂(SMe₂)₂] reaction with C₅H₅NO in C₂H₅OH.

Figure 5 shows the curves in all three solvents. We can get the thermodynamic parameters using the Van't Hoff equation. The results are shown in table 2.

Figure 5. The plot of $\text{Ln} K_{\text{eq}}$ vs. $1/T$ for $\text{cis-}[\text{Pt}(p\text{-Tol})_2(\text{SMe}_2)_2]$ reaction with $\text{C}_5\text{H}_5\text{NO}$ in different solvent.

Table 2. Thermodynamic Parameter Values for $\text{cis-}[\text{Pt}(p\text{-Tol})_2(\text{SMe}_2)_2]$ reaction with $\text{C}_5\text{H}_5\text{NO}$ at various temperatures in ethanol, acetone and benzen at 25°C .

Solvent	Ethanol	acetone	benzen
$\Delta H^\circ/(\text{J.mol}^{-1})$	6441.69	43100	46247
$\Delta S^\circ/(\text{J.mol}^{-1}.\text{K}^{-1})$	89.82	218.5	236
$\Delta G^\circ/(\text{kJ.mol}^{-1})$	-20.32	-22.013	-24.081

ΔH° , ΔS° and ΔG° are enthalpy, entropy and Gibb's energy of the reaction.

The results in table 1 and 2 show that the equilibrium constants and Stability constants are dependent on the solvent and the trend is related to the donor number of them. The Gutmann donor number for benzene, acetone and ethanol are 1, 17, and 31.5 respectively. The equilibrium constants for ethanol are smaller than acetone and benzene. Therefore, the equilibrium constant decreases with increasing the donor number. In other words, the four-coordinated complex was found to be more stable in a solvent with a higher donor number. Consequently, the trend for this influence on the reactivity of the studied complex toward a given N-donor is as below:

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