

Dimethyl sulfide for 3-carboaldehyde pyridine displacement in a platinum(II) Complex: Donor Number Effect

Alireza Akbari

Chemistry Department, Payame Noor University, 19395-4697 Tehran, Iran

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Abstract

The thermodynamic parameters and equilibrium constant for displacement of dimethyl sulfide by 3-carboaldehyde pyridine as N-donor ligand in *cis*-[Pt(4-MeC₆H₄)₂(SMe₂)₂] complex have been measured using UV-vis spectroscopy in acetone, dichloromethane and benzene at various temperatures (T=15-20 °C), and compared with my previously reported reactions. ΔH° (KJ.mol⁻¹) of the mentioned reaction in acetone has been 7.158 while obtained less in dichloromethane (4.109) and more in benzene (9.96). The entropy of the reaction has been obtained 86.86 J.mol⁻¹.K⁻¹ in acetone, while calculated less in CH₂Cl₂ (73.29 J.mol⁻¹.K⁻¹) and more in the last solvent (97.40 J.mol⁻¹.K⁻¹). Furthermore, the Gibbs energy, ΔG (J.mol⁻¹), of the reaction obtained -18738.79, -17741.55 and -19043.06 respectively, with the same order. In all three solvents, the values of enthalpy and entropy changes have been positive and decreased as the donor number of the solvents decreased.

Keywords: Platinum; thermodynamic; 3-carboaldehyde pyridine; donor number.

Introduction

Platinum-based compounds are widely used as chemotherapeutics for the treatment of various cancer sicknesses [1-3]. It is believed that the antitumor activity of cisplatin and

other platinum based drugs arise from their interaction with DNA [4]. For this reason, substitution reaction at square planar Pt(II) centers, have been extensively studied [5-8]. As a base phenomenon, high trans effect of a

*Corresponding author: Alireza Akbari

Tel: +98 (915) 3114323, Fax: +98 (51) 38528520

E-mail: a_akbari@pnu.ac.ir

σ carbon causes the rapid substitution processes for the ligand trans to it.

In this look, it was of interest to me to investigate a system containing σ -carbon trans directing to the leaving groups ligands. So many studies could be found in the areas such as steric effects of bulky substituents [9], Dissociative substitution [10], oxidative addition [11,12] and reductive elimination reactions [13], geometrical isomerization [14], electrophilic attack at the metal-carbon bond and exchange reactions [15]. These settled fields of study could be thought about from thermodynamic to kinetic characteristics of chemical reactivity of platinum or other metal complexes [16,17].

In the current study, I specify the thermodynamics of *cis*-[Pt(*p*-Tol)₂(3-carboaldehyde pyridine)₂] complex formation, starting by *cis*-[Pt(*p*-Tol)₂(SMe₂)₂] as initial complex, in which *p*-Tol = 4-MeC₆H₄. I then obtain the thermodynamic parameters for the ligand exchange of this reaction in three mentioned solvents with various donor numbers. Furthermore, I compared the results with my previous reported about similar reaction [18].

Experimental

The compounds 3-carboaldehyde pyridine, acetone, dichloromethane, and benzene were

of analytical level. The *cis*-[Pt(*p*-Tol)₂(SMe₂)₂] complex was arranged as formerly reported [19] and mentioned again in my previous work [18]. As a typical experiment in thermodynamic studies, the initial complex (2×10^{-4} mol.L⁻¹) was used and 3-carboaldehyde pyridine (0.05 mol.L⁻¹) was added stepwise. Keq values were extracted by fitting of obtained data using the KaleidaGraph software [20]. All UV-vis spectra were obtained using a Shimadzu-2550 spectrophotometer combined with temperature controller bath instrument, AYAT. Similar to what I described before [18], 3ml of initial complex (2×10^{-4} mol.L⁻¹ in acetone) 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 acetone) was added stepwise as in regular thermodynamic studies. Keq values were extracted using the fitting of obtained data.

Results and discussion

Reaction begins after the first ligand injection into the cell. Monitoring of the product concentration was carried out by comparing the related UV-vis spectra. Overlapping the spectra shows the existing of equilibrium between the reactants. In any next injections, according to Le Chatelier principle, the

equilibrium reactions get out of equilibrium, and after a few minutes, it gets equilibrium again and confirms by overlapping of the spectra. The reaction is nearly completed in the final injection. Overlaying all the spectra of each group in the last injection (in CH₂Cl₂ at T=17.5°C) has been shown in Figure 1.

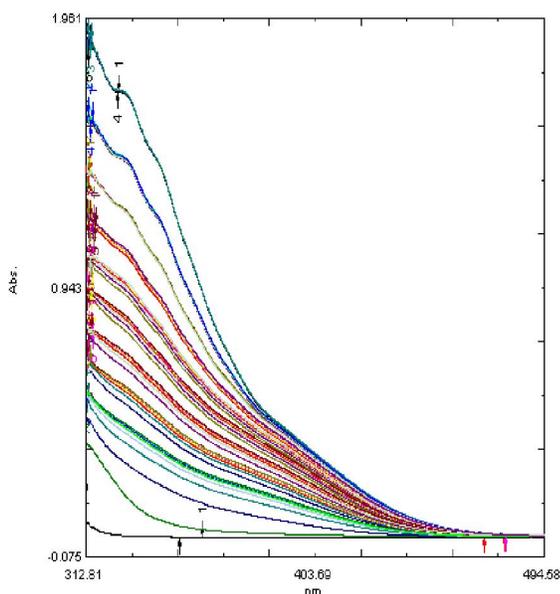
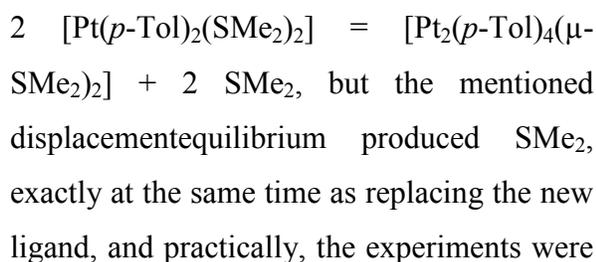


Figure 1. Electronic spectra of the reaction in CH₂Cl₂ at T=17.5 °C (molarities of entering ligand varied from each serial to next)

Although there is evidence for some dissociation of the [Pt(P-Tol)₂(SMe₂)₂] complex in solution[10] according to the following equilibrium:



done in the present of excess SMe₂. Using the data related to the last spectrum of each group and the ligand concentration, absorption plot is drawn. The fitting of the data is carried out using Kaliedagraph software and certain fitting equation, explained in my previous work [18], and the equilibrium constants are obtained.

After analyzing the different wavelengths, a suitable wavelength in each solvent is selected. The enthalpy and entropy of a reaction are affected by temperature changing, so by selecting the shorter range of temperatures, the more valuable results can be reached.

As an example, the fitted absorbance/concentration curves for ligand displacement at 385 nm in benzene and 12.5-20 °C are shown in Figure 2.

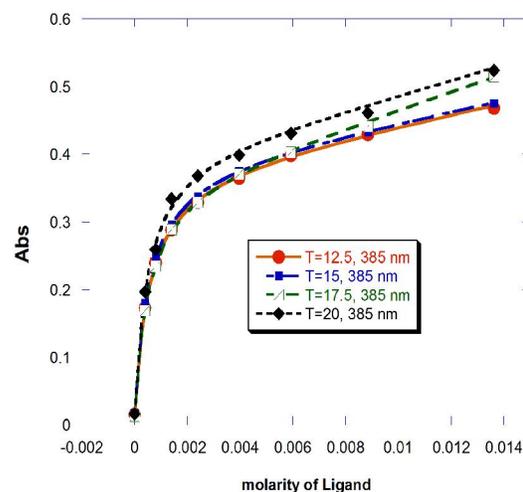


Figure 2. The plot (fitted) of Abs vs. molarity of the ligand at various temperatures in benzene

Noticing the plot and software fitting equation, the constant value of reaction equilibrium in temperature of 12.5 °C in dichloromethane solvent is 1192.8. After similar tests in 15, 17.5 and 20 °C and drawing and analyzing the plots, the equilibrium constants in mentioned solvents are obtained.

As it can be seen, when the temperature has risen, absorbance value in a certain concentration from ligand has increased too. The equilibrium constant values in this substituting reaction for various solvents at different temperatures have been presented in Table 1.

Table 1. Keq at various temperatures in three solvents

T (K)	285.65	288.15	290.65	293.15
Keq(CH ₂ Cl ₂)	1192.8	1211.5	1230.6	1246.3
Keq(CH ₃ COCH ₃)	1693.6	1734.5	1786.3	1827.1
Keq(C ₆ H ₆)	1818.9	1882.8	1953.5	2025.1

Using the different values of equilibrium constant in each solvent and various temperatures, the values of thermodynamic parameters can be found from Vant Hoff equation, $\ln K_{eq} = -\Delta H^0/RT + \Delta S^0/R$. Solvent has a direct effect on the speed of

formation and value of complex stabilization. Various specifications such as its dielectric constant and donor number, have important effectiveness. Generally, the results show that, in solvents with low dielectric constant, the complex stabilization reduced [21]. Donor number is the molecule specification of a solvent and is measured by calorimetry method. Although the Gutmann donor number is a right scale to the power of solvent for most chemical systems, it cannot be single suggestion for solvation power of solvents. Studies show that specific interaction between the solvent and solute is so effective in capability of solvent salvation [22-24]. As the solvent donor number is less, the amount of cation and ligand solvation is less, and complex formation is easier and consequently, the complex stability is more. On the contrary, in solvents with the high donor number due to the better solvation of cation and ligand, there are fewer possibilities for cation and ligand to be available to form the complex and consequently, the amount of complex formations reduce. Figure 3 shows the curves of $\ln K_{eq}$ vs. $1/T$ in three different solvents and calculated thermodynamic parameters containing the solvent donor numbers are listed in Table 2.

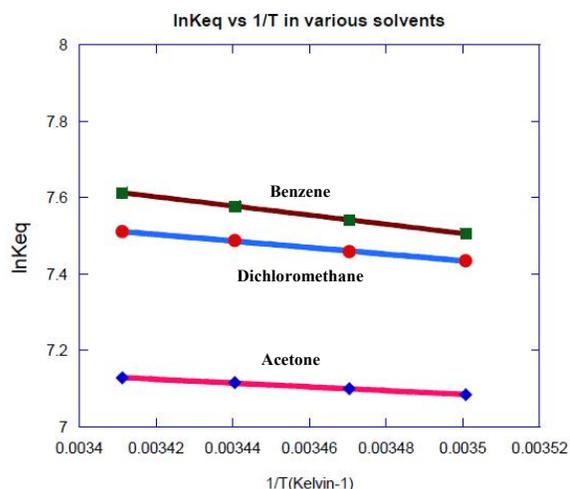


Figure 3. Eyring plots in three different solvents

Table 2. Donor No. and calculated thermodynamic parameter

Solvent	CH ₂ Cl ₂	CH ₃ COCH ₃	C ₆ H ₆
ΔH ⁰ (Jmol ⁻¹)	4109.86	7158.52	9996.75
ΔS ⁰ (JK ⁻¹ mol ⁻¹)	73.29	86.86	97.40
ΔG ⁰ (KJmol ⁻¹)	-17.76	-18.74	-19.04
Donor No.	30	17	1

Conclusion

The Gibb's energy for the same solvents in my previous report was -22.01 and -24.08 KJmol⁻¹ for acetone and benzene respectively [18]. Comparing the results showed that 3-carboaldehyde pyridine has more tendencies than pyridine-3-ol to binding the platinum complex.

Considering the data of table 2, one can find that the lower the donor number of solvent, the more positive the enthalpy change. It means that the reaction is more exothermic when the donor number increased. Considering this fact the reaction is done in solution phase, it should be considered that the total enthalpy change is the sum of two separate parts[25]:

$$\Delta H^0 = \Delta H^i + \Delta H^s$$

ΔHⁱ has a positive mark for this reaction and the reaction in gas phase is endothermic, because the two stronger bonds, Pt-S, are broken and two weaker bonds, Pt-N, are formed. ΔH^s, related to the solvation of the species, is the heat of an exothermic process and contains a negative mark. Noticing that as the solvent has more donor numbers, the value of solvation (especially for the species of this reaction, which are also polar) increases and ΔH^s becomes more negative and totally, ΔH⁰ gets smaller for the more polar solvent which has more donor number. By lowering the solvent donor number, the value of entropy has also increased and reaction in the solvent with a smaller donor number contains more entropy change. In this case again, due to the reaction is done in solution phase, it should be considered that ΔS⁰ = ΔSⁱ + ΔS^s. The value of ΔSⁱ for this reaction contains a positive mark, since the

species of SMe_2 as the product enters the gas phase and increases the entropy. As well as by increasing the donor number of solvent, the solvation value increases and consequently, the ΔS^\ddagger value for the solvent with a larger donor number will be less than the others.

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