Kinetic Study on 1,10-Phenantroline Reaction with Cis-[Pt(p-FC6H4)2(SMe2)2] Complex

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Abstract To determine the rate constants and kinetic parameters on the reaction between 1 10-Phenantroline, as a bidentate ligand and cis-[Pt(p-FC6H4)2(SMe2)2] complex in acetone and benzene solvents, the reactions were monitored by UV-Vis spectrophotometer. The pseudo-first-order rate constants (k_{obs}=k_1+k_2[phen]) of the reaction were derived, and the values of the first and second order rate constants (k_1 and k_2) calculated using standard equations. The reactions were carried out in the range of 20 to 50 °C. The second-order rate constant dependency on the temperature was in agreement with the Arrhenius equation, providing the relevant plots to calculate the activation energy of all the reactions. The ΔH#(KJ.mol⁻¹) and ΔS#(J.mol⁻¹.K⁻¹) were obtained 28.677 and –165.9 respectively in benzene. These values were 56.723 and -72.2 respectively, in acetone. The product synthesizing was confirmed using elemental (CHN) and spectral (IR) analysis.

Keywords Pt(II) Complex, Substitution, UV-Vis Spectrophotometry, Activation Parameters, Kinetics

1. Introduction

Ligand substitution reactions on monomeric square planar platinum (II) complexes have been extensively studied. These complexes have shown low rates in their reactions comparing with other d⁸ square planar complexes of palladium, nickel, rhodium, iridium and gold. This property is particularly important in cancer chemotherapy of platinum (II) complexes, since this allows binding to cellular DNA before inactivation of the Pt (II) center by extra cellular binding sites such as S-donor residues. Some researchers have investigated and focused on the kinetics and mechanism of the interaction of platinum (II) complexes and bio-molecules with the aim of developing new family of metallличal pharmaceuticals. The ionic complexes [M(Ph₂PC₂H₄P(Ph)C₂H₄PPPh₃)X]Cl have been obtained in substitution reaction of related chloro-complexes with 1 equivalent of KX(X=I,CN). There has been a great interest in ligand substitution reactions of organoplatinum (II) complexes containing one or more Pt–C bonds, e.g. the ligand substitution or ligand exchange on organometallic substrates of the type cis-[PtR₂L₂] (R=Ph or Me; L=thioethers or dimethylsulfoxide). Rashidi et al. have studied widely about the kinetics and mechanism of ligand substitution reactions involving binuclear dimethylplatinum(II) complex containing N-donor ligands. Kinetics and mechanism of substitution and ring opening reaction of some platinum(II) complexes with N-heterocyclic bases have been studied by UV–Vis spectrophotometry. There is evidence for a dissociative mechanism as well as associative in ligand exchange and substitution at platinum(II) complexes. Neutral monodentate ligands such as pyridine, 4-Me-pyridine and thiourea have been substituted with a SMe₂ ligand in the first step of reaction in trans-[PtClMe(SMe₂)₂] complex, as confirmed by ¹H NMR spectroscopy and kinetic data. It has been proven that ligand substitution processes trans to a carbon atom are extremely rapid due to the high trans effect of these ligands. In addition to the large trans effect of σ-carbon ligands, it is also well known that these ligands exert an appreciable trans influence by weakening the metal-ligand bond opposite on it. In this regard, we are interested in studying about the kinetic of the systems containing α-carbon trans directing ligand. Details of our findings in a comprehensive study of the substitution rates in the cis-[Pt(p-FC₆H₄)₂(SMe₂)₂] complexes reactions with 1 10-Phenantroline, as a neutral bidentate ligand are reported in this paper.

2. Experimental

2.1. Materials and Instrumentation

The ligand, 1,10-phanthreline, was a Merk product. Acetone and benzene, used as the solvents were purchased from the Merk or Fluka Company. All UV-Vis spectra were recorded in a Shimadzu double beam spectrophotometer machine, UV–Vis 2550. Sartorius analytical balances with accuracy 0.0001, a micro syringe 500 mL, and a screw cap cuvette made by American Hellma Company, were used for
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experiments. In all measurements, a circulator Ayat 83 was used for controlling the temperature.

The infrared spectrum was recorded on a Shimadzu Prestige 8400 FT-IR spectrometer as KBr disks. CHN analysis was performed using a Heraeus CHN-O-FLASH EA 1112 elemental analyzer.

2.2. Synthesis of Platinum Complexes

In order to synthesis of the first complex, FC₆H₄MgBr was used as reported. The reaction between (p-FC₆H₄)₂MgBr and [PtCl₂(SMe₂)₂] was occurred and led to synthesis of Cis-[Pt(p-FC₆H₄)₂(SMe₂)₂]. Related reaction is appeared in following:

\[
cis/trans-PtCl₂(SMe₂)₂ + 2(p-FC₆H₄)₂MgBr \rightarrow cis-[Pt(p-FC₆H₄)₂(SMe₂)₂] + PtCl₂(SMe₂)₂ + 2(p-FC₆H₄)₂MgBr
\]

All properties such as ¹HNMR chemical shifts of this precursor were similar to be reported.

In a substitution reaction which is shown in Figure 1, two dimethyl sulfide ligands are substituted slowly by a bidentate 1, 10-Phenanthroline, ligand.

Figure 1. Substitution reaction of 1,10-Phenanthroline with [Pt(p-FC₆H₄)₂(SMe₂)₂].

A solution of 1,10-phenanthroline (5 mmol, 0.9 g) in 50cc acetone was added to a solution of Cis-[Pt(p-FC₆H₄)₂(SMe₂)₂] complex (5 mmol, 2.55 g) in 50 ml of the same solvent. The mixed solution was stirred for 72h in a closed flask. Immediately, after opening the flask, smell of the released SMe₂ was distinguished. The yellowish precipitate was filtered, washed with ether (3×5 ml) and dried in vacuum.

CHN analysis for C₂₄H₁₆F₂N₂Pt (%): C, 50.12; H, 2.84; N, 4.75. Significant IR bonds (KBr, cm⁻¹): 3421.5 s (υ=C-H), 1625.9 w (υ=C=N), 1473.5 s (υ=C=C), 1384 s (υ=C-N), 813.9 m (υ=C-H), 582.5 w (υ=Pt-C), 518.8 w (υ=Pt-N).

2.3. Kinetic Methods

Kinetics of irreversible reaction shown in Figure 1 was studied using UV–Vis spectrophotometry technique. Analysis of the curves were done using Excel and KaleidaGraph softwares. The aim of this study is the determination of kinetic parameters (ΔH#, ΔS#) in acetone and benzene solvents, and we don't study the mechanism of the reaction. Following ordinary equations were used:

\[
\text{Ln}(k_2/T) = \text{Ln}(k_B/h) + (\Delta S# / R) - (\Delta H# / RT) \quad \text{(Eyring equation)}
\]

\[
K_{obs} = k_1 + k_2 [\text{Phen}]
\]

in which, k₁, k₂ and K_{obs} are the dissociative path (so-called solvent-assisted), the associative and pseudo-first-order rate constants respectively. R, h and K_B are the ideal gas, Plank and Boltzmann constants respectively.

3. Results and Discussion

This reaction could be a pseudo-first-order one, if we use the exess concentration for one of reagents, so the concentration of new ligand should be at least tenfold of primary complex concentration in each run. As an example, 300 µL of 1,10-Phenanthroline(0.0038538 molL⁻¹) was added to 2 ml of the starting complex at a constant temperature (35 °C) in a screw cap cuvette and the absorbance of mixed solution were recorded until the reaction was finished. The results are displayed in Figure 2.

Figure 2. Absorption vs. wavelength in 35°C for adding 300 µL of new ligand in Acetone

In spite of produced complex case, the starting complex had no absorbance, so after a while, increase in absorbance was observed. After collection of the related absorption, which according to Beer-Lambert law (A=ε.b.c) should be
less than 1, the maximum wavelength, $\lambda_{\text{max}}$, was determined in $414.3\,\text{nm}$ (in acetone). Then, nonlinear curves of absorption against time of reaction were analyzed with pseudo-first-order method (Figure 3).

Figure 3. Absorption vs. time in $35^\circ\text{C}$ for adding $300\,\mu\text{L}$ of new ligand in Acetone

Pseudo-first-order rate constant of the reaction ($K_{\text{obs}}$) was obtained by nonlinear least–square fitting of absorption–time curve to a first order equation, $A_t = A_\infty + (A_0 - A_\infty)\cdot\exp(-K_{\text{obs}}\cdot t)$. As it can be see in sample curve (Figure 3), the curve fit (green) shows the good agreement with the main curve. The $m_1$ parameter is equal to $K_{\text{obs}}$, and $m_2$ is the difference between $A_0$ and $A_\infty$ and both of them have small errors. Using other concentrations of $1,10$–Phenanthroline in $35^\circ\text{C}$, similar results were obtained and gathered in Figure 4. The volumes of new ligand in this figure represent the used concentrations.

Figure 4. Overlay of absorption–time curves in Acetone, $T=35^\circ\text{C}$

The concentration of the primary complex in all experiments was $2.5\times10^{-4}\,\text{mollit}^{-1}$. The second-order rate constant ($k_2$) also was calculated by plotting of $K_{\text{obs}}$ values versus concentrations of $1,10$–Phenanthroline. The same method were used for other selected temperatures, including $20$, $30$ and $50\,^\circ\text{C}$ and the second-order rate constants of reactions were obtained. From Figure 5, we realize that the rate increases as temperature goes up from $20$ to $50^\circ\text{C}$.

Figure 5. Overlay of $K_{\text{obs}}$ against different concentrations of $1,10$–Phenanthroline in various temperatures(in Acetone)

| $T$ (Centigrade) | 20   | 30   | 35   | 38   | 50   |
|------------------|------|------|------|------|------|
| $1/T$ (Kelvin)   | 0.0034 | 0.0033 | 0.0032 | 0.0032 | 0.0031 |
| $k_2$            | 0.0928 | 0.1137 | 0.2572 | 0.5139 | 0.6903 |
| $\ln(k_2/T)$     | -8.0575 | -7.8886 | -7.0887 | -6.4060 | -6.1483 |
| $k_1$            | 0.0008 | 0.0023 | 0.0025 | 0.0025 | 0.0070 |

The data shows that the values of $k_2$ are around 100 fold of $k_1$ and it means that the dissociative path is negligible in acetone.

According to the obtained data from previous curves and using Eyring equation, Figure 6 is plotted and kinetic parameters are estimated. Slope and intercept of this curve are $-6822.6$ and $15.076$, respectively. $\Delta S^\circ$ and $\Delta H^\circ$ values were determined $-72.2\,\text{J.mol}^{-1}\cdot\text{K}^{-1}$ and $56.723\,\text{KJ.mol}^{-1}$ using the intercept ($k_1$) and slope ($k_2$), respectively.

Figure 6. Plot of $\ln(k_2/T)$ against $1/T$ in Acetone as solvent
Physical and chemical characteristics of solvents can cause variations in many reactions. In fact, changing the solvent has a considerable effect on stability of the formed complex. So, to finding the solvent effect, the same experiments and computations were done for benzene, and similar curves were drawn. \( \lambda_{\text{max}} \) was determined in 443 nm.

Some of the obtained second-order rate constants, \( k_2 \), and their related values in benzene, are shown in Table 2.

| \( T \) (Centigrade) | 25.5 | 27 | 30 | 39 |
|---------------------|------|----|----|----|
| \( 1/T \) (Kelvin)  | 0.0033 | 0.0033 | 0.0033 | 0.0032 |
| \( k_2 \)           | 0.1184 | 0.1320 | 0.1857 | 0.2095 |
| \( \ln(k_2/T) \)     | -7.8328 | -7.7295 | -7.3977 | -7.3065 |
| \( k_1 \)           | 0.0003 | 0.0003 | 0.0002 | 0.0002 |

According to the obtained data from previous curves and using Eyring equation, Figure 7 was plotted and kinetic parameters were estimated.

The slope and intercept of this curve were obtained \(-3449.3 \) and \( 3.80 \), respectively. \( \Delta S^\# \) and \( \Delta H^\# \) values were determined \(-165.9 \) J.mol\(^{-1}\)K\(^{-1}\) and \( 28.677 \) KJ.mol\(^{-1}\) using the intercept and slope respectively. Obtained kinetic parameters, \( \Delta H^\# \) and \( \Delta S^\# \), for both solvents are given in Table 3.

| Kinetic parameters | Benzene | Acetone |
|--------------------|---------|---------|
| \( \Delta S^\# \) (J.mol\(^{-1}\)K\(^{-1}\)) | \(-165.9\) | \(-72.2\) |
| \( \Delta H^\# \) (KJ.mol\(^{-1}\)) | \(28.677\) | \(56.723\) |

**Table 2.** First and second order rate constant in Benzene

**Table 3.** Kinetic parameters in benzene and acetone

According to previous discussed points, the reaction mechanism of cis-[Pt(p-FC\(_6\)H\(_4\))\(_2\)(SM\(_2\)\(_2\)\)] complex with 1,10-phenanthroline is depicted in Figure 8.

**Figure 7.** Plot of \( \ln(k_2/T) \) against \( 1/T \) in Benzene as solvent

Furthermore, \( p\)-FC\(_6\)H\(_4\) is a \( \pi \)-acceptor and it can labilize the SM\(_2\) ligand. When such ligand forms strong \( \pi \) bond with Pt, the energy of the transition state is to be lower, and the activation energy is reduced.

As one can see, the parameters are almost the same, and in fact, although we expected more dissociative path in benzene (for substitution of bidentate ligand phenanthroline), but a negative value of \( \Delta S^\# \) indicates that the associative path is in current for benzene as well as acetone.

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