

Determination of Reaction Kinetic Parameters from Variable Temperature Kinetic Study for Oxidative Addition Reaction on Binuclear Cyclometalated Platinum(II) Complexes

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The pseudo-first order rate constants and activation parameters have been determined using two methods, constant-temperature kinetic (CTK) and variable temperature kinetic (VTK), for the oxidative addition reactions of $[\text{Pt}_2\text{Me}_2(\text{C}^{\wedge}\text{N})_2(\mu\text{-dppf})]$, (1a, $\text{C}^{\wedge}\text{N}$ = deprotonated 2-phenylpyridine (ppy); 1b, $\text{C}^{\wedge}\text{N}$ = deprotonated benzo[h]quinoline (bhq)) with MeI. The results obtained from VTK method are in agreement with those obtained at CTK method, but there are significant advantages to determine the kinetic reaction parameters under VTK method including time and chemicals saving.

Keywords: Oxidative addition, Platinum, Kinetic study, Variable temperature kinetic, Mechanism

INTRODUCTION

Oxidative addition is a fundamental reaction for many applications of organometallic compounds in many industrially important catalytic reactions [1-4]. During last three decades, this type of reaction, including the oxidative addition reactions of organic halides to mononuclear platinum(II) complexes, has widely been studied [5-9]. The classical $\text{S}_{\text{N}}2$ type mechanism and a second order rate law (*i.e.* rate = $k_2[\text{complex}][\text{halides}]$) has usually been suggested for these reactions, although in some cases a radical mechanism has also been observed [2]. Despite many reports on the oxidative addition reactions of alkyl halide to mononuclear Pt(II) complexes, related oxidative addition reactions involving binuclear platinum(II) complexes have not been studied much [10-13].

The oxidative addition reactions on dimeric Pt(II) complexes are important because there may be a cooperative steric and electronic effects between the two adjacent platinum centers [14-17]. The report of

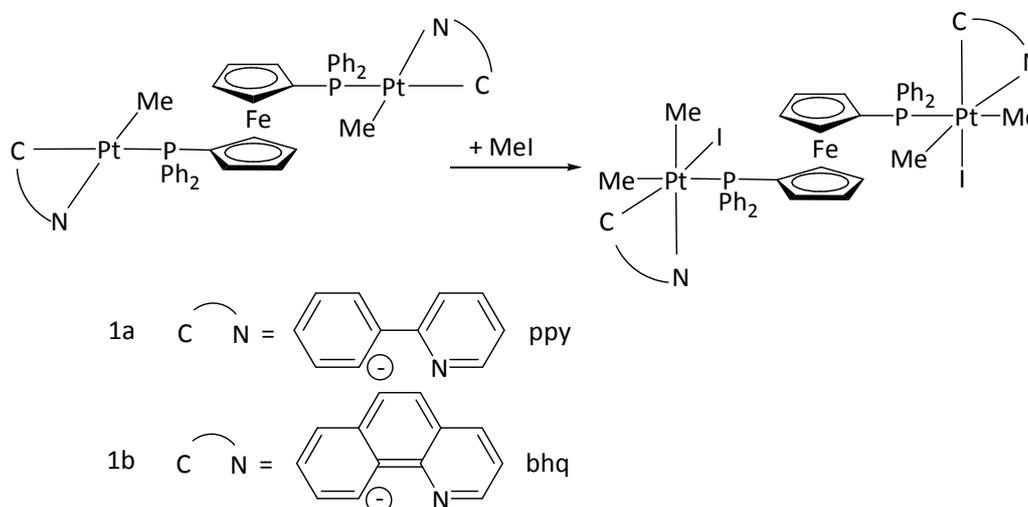
oxidative addition of MeI to a binuclear cycloplatinated(II) complex containing a bridging biphosphine ligand dppf (= 1,1'-bis(diphenylphosphino)ferrocene) showed a stepwise oxidative addition of the reagent to the platinum(II) centers [18].

Generally, the kinetic of oxidative addition reactions to platinum(II) complexes is studied using pseudo-first-order technique and the pseudo-first-order rate constants (k_{obs}) are evaluated by nonlinear least-squares fitting of the absorbance-time data to the first-order equation (Eq. (1)).

$$\text{Abs}_t = \text{Abs}_{\infty} + (\text{Abs}_0 - \text{Abs}_{\infty}) \exp(-k_{\text{obs}}t) \quad (1)$$

Graphs of these pseudo-first-order rate constants against the concentration of the added reagents, such as MeI, usually give good straight-line plots passing through the origin, showing a first-order dependence of the rate on the concentration of the reagent. Thus, the overall second-order rate constants (k_2) are determined from the slope of these graphs. To obtain activation parameters (ΔH^{\ddagger} and ΔS^{\ddagger} , Eyring equation, Eq. (2)), which are required to suggest a reaction mechanism, the same method is used at other temperatures.

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Scheme 1. Reaction studied in the present work

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (2)$$

The method explained in the last paragraph, named as constant-temperature kinetic or CTK, has been applied extensively for oxidative addition reactions during the past several decades. Nowadays, another technique named the variable-temperature kinetic (VTK) [19-23] has been used for reactions such as substitution and isomerization reactions. Considering some advantages of VTK against CTK, in the present investigation, we report the use of variable-temperature kinetic (VTK) technique for oxidative addition reactions of MeI on binuclear cyclometalated Pt(II) complexes and compare our results with those obtained from constant-temperature kinetic or CTK method. Particularly, we have determined the reaction kinetic parameters for oxidative addition reactions of $[Pt_2Me_2(C^N)_2(\mu-dppf)]$, (see Scheme 1: 1a, $C^N =$ deprotonated 2-phenylpyridine (ppy); 1b, $C^N =$ deprotonated benzo[h]quinoline (bhq)) with MeI under variable-temperature kinetic conditions. The reactions were followed easily by using UV-Vis spectroscopy under VTK, savings time and chemicals. No loss of accuracy in the obtained kinetic parameters has been observed, when compared to kinetic data obtained under pseudo-first-order conditions by CTK method. Therefore, we suggest this technique to use for investigation of other oxidative addition

reactions involving d^8 square planar transition metal complexes.

EXPERIMENTAL

The starting binuclear cyclometalated platinum(II) complexes, $[Pt_2Me_2(C^N)_2(\mu-dppf)]$, (1a, $C^N =$ ppy [12]; 1b, $C^N =$ bhq [18]) have been prepared and characterized according to literature. The starting complexes, used for kinetic investigations, were separated as solids and dried under vacuum. The Perkin-Elmer Lambda 25 spectrophotometer was used for kinetic study of oxidative addition reactions under both methods, CTK and VTK techniques.

In the CTK method [18], a solution of cycloplatinated(II) dimer in chloroform (3 ml, 3×10^{-4} M) was thermostated at 25 °C, and a known excess of the MeI was added using a microsyringe. After rapid mixing, the change in absorbance of cyclometalated platinum(II) solution at suitable wavelength was monitored with time and the absorbance-time curves were investigated by nonlinear least-squares fitting of the absorbance-time profiles to a first-order equation (Eq. (1); Fig. 1) from which the observed first-order rate constants (k_{obs}) were determined. A plot of k_{obs} versus concentration of MeI was linear, and the slope gave the second-order rate constant. During the kinetic experiments, temperature was carefully

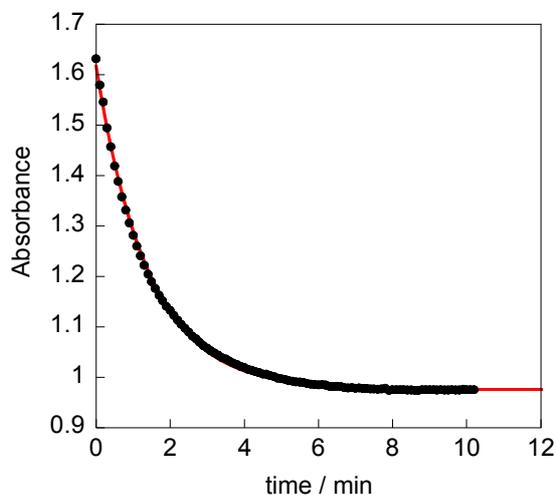


Fig. 1. The plot shows the time course of absorbance for the reaction of 1b with MeI in CHCl₃ at 25 °C.

Table 1. Rate Constants^a and Activation Parameters for the Reaction of the Diplatinum(II) Complexes with MeI in CHCl₃ Using Constant- and Variable-temperature Kinetic Methods

	1a		1b	
	10 ² <i>k</i> ₂ (M ⁻¹ s ⁻¹)		10 ² <i>k</i> ₂ (M ⁻¹ s ⁻¹)	
	CTK ^b	VTK	CTK ^c	VTK
T = 10 °C	1.11	1.27	0.79	0.81
T = 15 °C	1.57	1.63		
T = 20 °C	2.17	2.13	1.56	1.58
T = 25 °C	3.00	3.08	2.15	2.31
T = 30 °C	3.79	3.94	3.39	3.49
ΔH^\ddagger (kJ mol ⁻¹)	41.8 ± 1.2	38.9 ± 1.9	49.9 ± 2.4	49.2 ± 2.6
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-134 ± 4	-143 ± 6	-109 ± 8	-111 ± 9

^aEstimated errors in *k*₂ values are ± 5%. ^bData from ref. [12]. ^cData from ref. [18].

controlled by using an EYELA NCB-3100 instrument. The same method was used at other temperatures, and activation parameters were obtained from the Eyring equation (Eq. (2)). The results are shown in Table 1.

In the VTK method, temperature was carefully increased and controlled by a programmable temperature bath (EYELA NCB-3100). This instrument increases the temperature with time with an accuracy of ±0.1 °C. The

procedure for kinetic study of oxidative addition reactions was same as described previously for the CTK method. The absorbance-temperature-time data were automatically acquired by using a Visual Basic program. The initial temperature (T_0) was adjusted at sufficiently low, 276 K, to slow down the initial rate of the reaction. The MicroMath SCIENTIST program [24] was used for processing of the obtained data and the Euler method was used for solving the differential Eq. (3).

$$-\frac{d(A_t - A_\infty)}{dt} = \frac{k(T_0 + \alpha t)}{h} \exp\left[\frac{\Delta S^\ddagger}{R}\right] \exp\left[-\frac{\Delta H^\ddagger}{R(T_0 + \alpha t)}\right] (A_t - A_\infty) \quad (3)$$

In Eq. (3), T_0 is the initial temperature, α is the temperature gradient, A_t and A_∞ are the absorbance at the time t and the absorbance at completion of the reaction, respectively. This equation was used to determine ΔH^\ddagger and ΔS^\ddagger parameters. Figure 2 shows a variable-temperature kinetic run for the reaction of complex $[\text{Pt}_2\text{Me}_2(\text{bhq})_2(\mu\text{-dppf})]$ with MeI in CHCl_3 with a linearly increasing temperature $T = T_0 + \alpha t$ with $T_0 = 276.0 \pm 0.1$ K and $\alpha = 0.0083 \pm 0.0001$ K s^{-1} .

RESULT AND DISCUSSION

Two methods, constant-temperature kinetic (CTK) and variable-temperature kinetic (VTK) are used for kinetic studies of the oxidative addition reactions of binuclear cycloplatinated(II) complexes $[\text{Pt}_2\text{Me}_2(\text{C}^{\wedge}\text{N})_2(\mu\text{-dppf})]$, (Scheme 1: 1a, $\text{C}^{\wedge}\text{N} = \text{ppy}$; 1b, $\text{C}^{\wedge}\text{N} = \text{bhq}$) with MeI and the data obtained from these methods are compared.

CTK Method

The UV-Vis spectra of yellowish binuclear complexes 1a and 1b contain metal to ligand charge transfer bands in the visible region. These MLCT bands are used to study the kinetics of their reactions with MeI by using UV-Vis spectroscopy. According to CTK method, an excess of MeI was added to a CHCl_3 solution of cyclometalated Pt(II) complexes at corresponding temperature and the decreasing in the absorbance related to the MLCT bands was used to follow up the reaction. A typical run is shown in Fig. 1. The pseudo-first-order rate constants (k_{obs}) were calculated by fitting of the absorbance-time profiles according to Eq. (1).

From the slope of plots of the pseudo-first-order rate constants, k_{obs} , versus concentration of MeI, the second-order rate constant (k_2) was obtained. The results for oxidative addition reactions of both cyclometalated Pt(II) complexes with MeI are collected in Table 1. The order of the reaction is two, first order in both the corresponding dimer complex and MeI. This procedure was repeated at other temperatures for determination of the enthalpy and entropy of activations. Data are shown in Table 1.

VTK Method

In this case, the preparation of solutions for kinetic study of the reactions shown in Scheme 1 was similar to that described above for CTK method. Considering very important role of temperature in this method, the temperature was carefully controlled by programmable temperature bath instrument.

The starting temperature (T_0) was 276 K which is sufficiently low to reduce speed of the initial rate of the reaction. After addition of MeI to solution of cyclometalated Pt(II) complexes, the temperature increased linearly according to the general equation $T = T_0 + \alpha t$. The reactions were followed by monitoring the disappearance of MLCT bands and abs-time data were collected using appropriate software. The SCIENTIST program [20] was used for processing of the abs-time-temperature data. From the data analysis using the differential equation (see Eq. (3), and Fig. 2), the values of the rate constants and enthalpy and entropy of activation for the oxidative addition reaction of 1a and 1b with MeI are obtained and collected in Table 1. It should be noted that, using VTK method, all the reaction kinetic parameters including rate constants at different temperatures, enthalpy and entropy of activations are obtained only in a single kinetic run.

As can be seen from Table 1, the rate constants for oxidative addition of MeI to binuclear cyclometalated platinum(II) complexes (see Scheme 1), obtained from VTK method, are in very good agreement with the data obtained from CTK method. There is also good agreement between the values of enthalpy and entropy of activations obtained by the VTK method with those obtained by CTK method.

The determination of kinetic parameters by the VTK method for oxidative addition reactions of platinum dimers with MeI and comparing the results with those

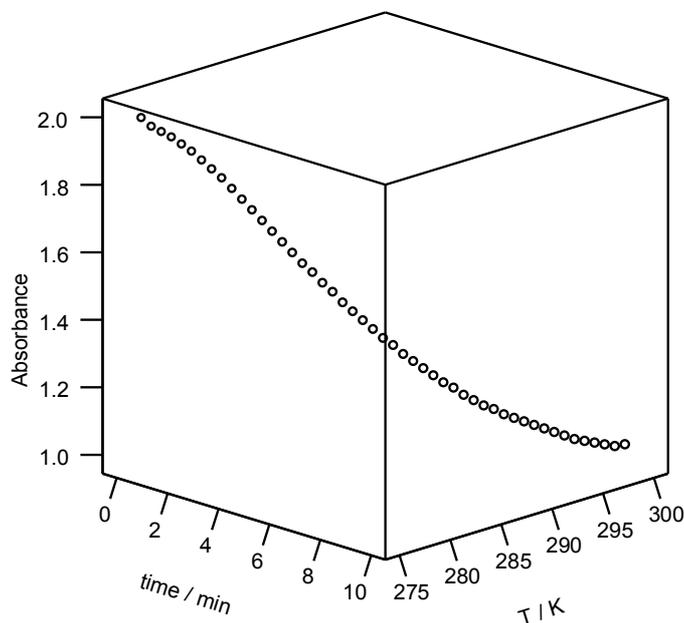


Fig. 2. Absorbance changes as a function of time and temperature during the oxidative addition of 1b with MeI in CHCl_3 at variable temperature $T = 276 \pm 0.0083 \times t$.

obtained from CTK method has shown that the VTK method can be easily used instead of the traditional CTK method.

Several factors such as concentrations of the chemicals and also time measurements are important for kinetic studies of the reactions. As can be seen from the results presented in Table 1 for CTK and VTK methods, VTK method has several advantages: (i) using VTK method, it is possible to shorten the time needed for determination of kinetic parameters, therefore the measurements would be fast and easy; (ii) all kinetic parameters such as rate constants and enthalpy and entropy of activations can be obtained only in one single kinetic experiment, compared to at least 20 experiments used for CTK method and (iii) using VTK with a single kinetic run, it is possible to save time and chemicals needed for kinetic study, especially for expensive transition metal compounds which are consumed during the kinetic experiments.

CONCLUSIONS

Usually in constant-temperature kinetic (CTK) method, the time needed for kinetic studies of the reactions to determine all kinetic parameters (such as rate constants,

enthalpy and entropy of activations) is so long. Also a large amount of materials has usually been needed, under pseudo-first order condition, in order to follow the kinetics of the reactions. These factors are not appropriate for kinetic studies of expensive transition metal complexes. However, as presented in this work, by using variable-temperature kinetic (VTK) method, the rate of the oxidative addition reaction of MeI to dimeric platinum(II) complexes $[\text{Pt}_2\text{Me}_2(\text{C}^{\wedge}\text{N})_2(\mu\text{-dppf})]$, ($\text{C}^{\wedge}\text{N} = \text{ppy}$ or bhq) and enthalpy and entropy of activations can be easily determined from a single experiment at a wider temperature range. Therefore, we suggest that the VTK method can successfully be applied for oxidative addition reactions saving significantly time and chemicals.

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