RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.2, No.4 (2009), 924-934
ISSN: 0974-1496
CODEN: RJCABP

KINETICS AND MECHANISM OF THE INTERACTION OF L-CYSTEINE WITH DI-μ-HYDROXOBIS(1,10-PHENANTHROLINE)DIPALLADIUM(II) ION IN AQUEOUS SOLUTION

Goutam K. Ghosh and Sankar Chandra Moi∗
Department of Chemistry, National Institute of Technology, Durgapur-713209, India∗Author for
E-mail: sankarmoi67@yahoo.com

ABSTRACT

Kinetics of interaction between L-cysteine with the di-μ-hydroxobis(1,10-phenanthroline)dipalladium(II) ion complex has been studied spectrophotometrically as a function of $[Pd(1,10\text{-phen})(H_2O)_2]^{2+}$, *[L-cysteine], pH and temperature. The reaction has been monitored at* λ_{max} *240 nm. The reaction rate increase linearly with increase in [L-cysteine] in the studied concentration range. The second order rate constants for the two step process are in the order of* $k_1 \approx 10^{-5} dm^3 mol^{-1} s^{-1}$ *and* $k_2 \approx 10^{-3} dm^3 mol^{-1} s^{-1}$ *respectively. The activation parameters calculated from Eyring plot are* $\Delta H_1^{\ddagger} = 75.22 \pm 3.58$ *KJ mole*$^{-1}$, $\Delta S_1^{\ddagger} = -98.94 \pm 4.67 JK^{-1}mole^{-1}$, $\Delta H_2^{\ddagger} = 68.81 \pm 3.22$*KJ mole*$^{-1}$, $\Delta S_2^{\ddagger} = -110.27 \pm 5.26\ JK^{-1}mole^{-1}$. *On the basis of the kinetic and activation parameters an associative mechanism is proposed for the interaction process.*

Key words: Kinetics and mechanism, L-cysteine, 1,10-phenanthroline, associative mechanism, hydroxo bridge palladium(II) complex.

INTRODUCTION

Cis-platin, $[Pt(NH_3)_2Cl_2]$ was approved for the treatment of testicular and ovarian cancer[1] in 1978 as a phase1 clinical purpose but its applicability is still limited to relatively narrow range of tumors. For the kinetic and mechanistic investigation of the mechanism action of platinum(II) anticancer drugs, their palladium(II) analogues are suitable models compounds since they exhibit a 10^4-10^5 fold higher reactivity, whereas there structural and equilibrium behaviour are rather similar[2]. Our interest mainly focused on the steric and electronic effect to tune the acidity and reactivity of such complex for their application as antitumor drugs[3-6]. The decrease in reactivity was induced by increasing the stearic hindrance on the amine ligands and attributed to the attacking side become blocked for incoming ligands. In this study a careful distinction between and variation of σ-donor and π-acceptor effect play an important role in controlling the reactivity of the complex[7, 8]. In $[Pd(1,10\text{-phen})(H_2O)_2]^{2+}$ ion complex, (where 1,10-phenanthroline is better σ-donor and π-acceptor property as well as steric ligand) remain as dimeric palladium(II) complex in the studied pH range, which is comparatively less labile than other studied palladium(II) complexes[9-11]. It is well known that the sulfur containing bio-active molecules may act as a drug reservoir[4] for platination at DNA. Moreover, the interaction of Pt(II) complexes with sulfur containing bio-active ligands has been associated with negative phenomena, such as nephrotoxicity, gastrointestinal toxicity, ototoxicity and neurotoxicity[12]. The importance of the work lies on the fact that the reaction has been studied in aqueous medium and we have selected aqua immine (1,10-phenanthroline) Pd(II) complex, which is better than chloro amine complexes (e.g. Cis-platin), since the hydrolysed side products of the chloro complex are toxic.

EXPERIMENTAL

The [Pd(1,10-phen)Cl_2] is prepared by following the standard literature method method[13]. The diaqua complex, [Pd(1,10-phen)$(OH_2)_2]^{2+}(ClO_4^-)_2$ is prepared in solution by method of Hay and Basak[14], by stirring the chloro complex with two mole equivalent of $AgClO_4$ and kept overnight (with careful protection from light). The precipitated AgCl was removed by filtration. The complex is characterised by UV-Visible spectroscopy (λ_{max} = 272 nm.) and elemental analysis[13], C = 35.6%(31.6), H = 2.3 % (2.4), N = 7.4% (7.3) and O = 17.8% (17.6). The reactant complex ion, di-μ-hydroxobis(1,10-phen)dipalladium(II) ion complex(**1**) is obtained in situ by adjusting the pH at 6.5 by adding $NaOH/HClO_4$. The reaction product of L-cysteine and complex1 is prepared by mixing them in different ratios, viz, 1:1, 1:2, 1:3, 1:5 and 1:10 and thermo stating at 50 ^{0}C for few hrs. The absorption spectra (Figure-1) exhibited the same λ_{max} irrespective of the ratio of the mixing. Its composition in solution is also determined by Job's method of continuous variation. The metal: ligand ratio is found to be 2:1 (Figure-2). The pH of the solution is adjusted by adding $NaOH/HClO_4$ and measurement is carried out with the help of systonics digital pH meter with an accuracy of ±0.1 units. Double distilled water is used to prepare all the solutions for kinetic measurement. All chemicals used are AR grade. The reactions are carried out at constant ionic strength (0.1M $NaClO_4$).

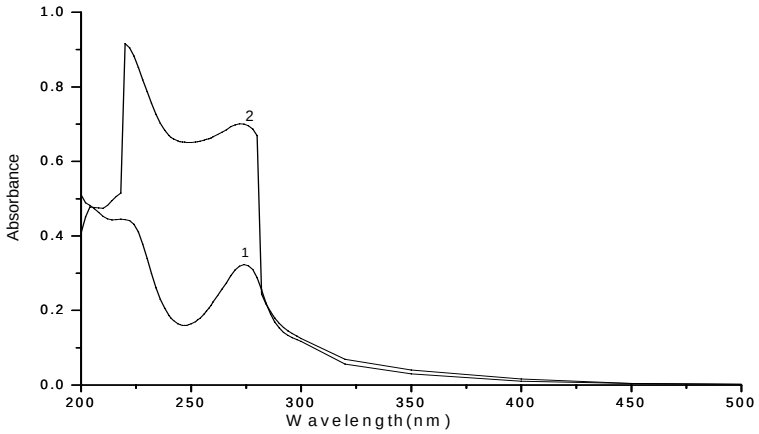
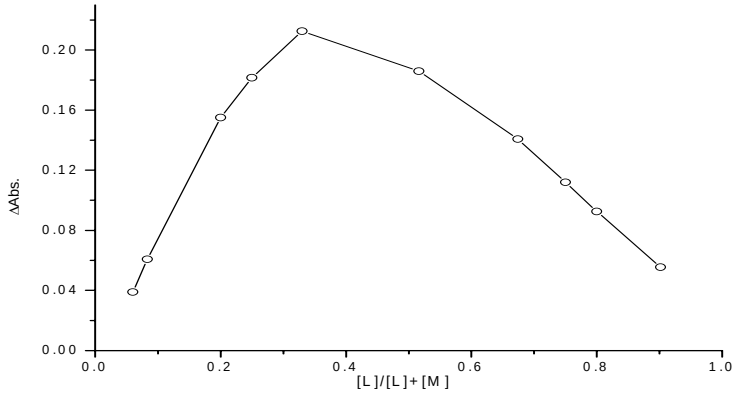


Fig.-1: Spectral difference between reactant and product,(1) $[Pd_2(1, 10\text{-phen})_2(OH)_2]^{2+}$ =4.135 x 10^{-4} mol dm^{-3}, (2) $[Pd_2(1,10\text{- phen})_2(OH)_2]^{2+}$ = 4.135 x 10^{-4} mol dm^{-3}, [L-cysteine] = 4.135 x 10^{-3} mil dm^{-3} pH= 6.5, cell used 1 cm. quartz.



, Fig.-2: Job's plot

Kinetics

Kinetic measurement are recorded on a Shimadzu UV1601 spectrophotometer attached with thermoelectric cell temperature controller (model TCC-240A), accuracy ± 0.1^0C. The conventional mixing technique is followed and pseudo-first order conditions are employed throughout the kinetic run. The progress of the reaction is followed by measuring the increase in absorbance at 240 nm, where the spectral difference between the complex(**1**) and the product complex is maximum. The plot of ln (A_∞- A_t) versus time t, where A_∞ and A_t are the absorbance at infinite time (after the completion of the reaction) and at time 't', are found to be non linear. The plot at the initial stage is linear with constant slope and subsequently it is curved in nature (Figure-3). The method of Weyh and Hamm[15] is adopted to calculate the rate constant for two consecutive steps. The $k_{2(obs)}$ values are obtained from the plot of lnΔ(the measuring of Δ is shown in the Figure- 3) versus time t (Figure-4). The rate data, represented as an average of duplicate runs are reproducible to within ± 4 %.

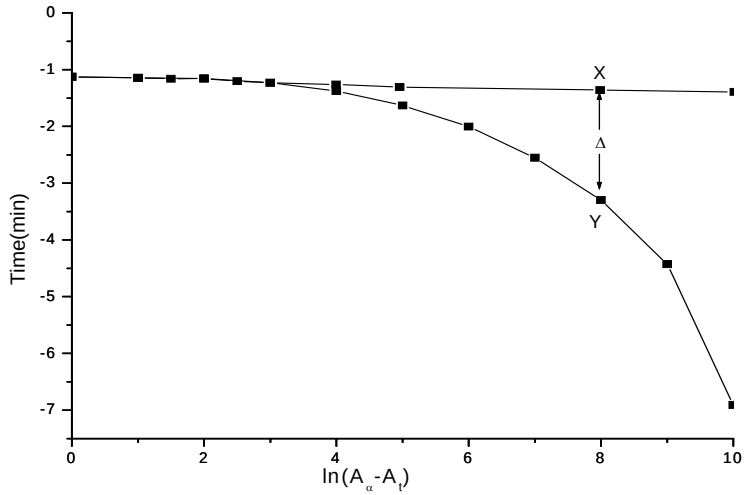


Fig.-3. A typical plot, of ln(A_α-At) versus, time(min), $[Pd_2(1,10\text{-phen})_2(OH)_2]^{2+}$= 4.135x 10^{-4} moldm^{-3}, [L-cysteine]= 8.27 x 10^{-3}moldm^{-3}, pH=6.5, temp. = 20 ^{0}C

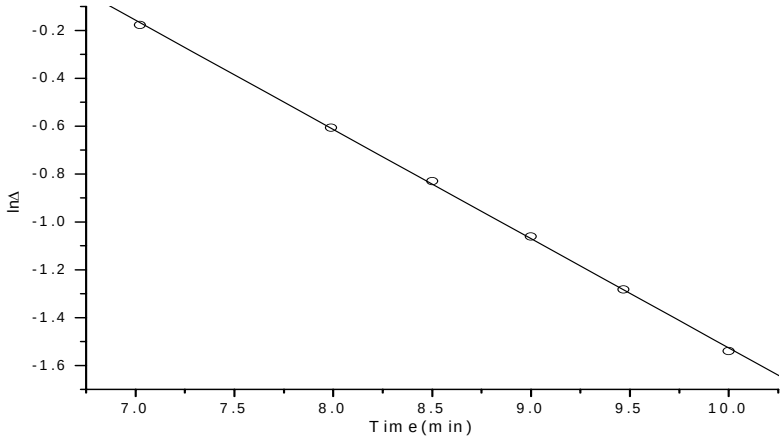


Fig.- 4. A typical plot of lnΔ versus time (min), $[Pd_2(1,10\text{-phen})_2(HO)_2]^{2+}$= 4.135 x 10^{-4}moldm^{-3} , [L-cysteine]= 8.27 x 10^{-3}moldm^{-3}, pH=6.5, temp. = 20 ^{0}C

RESULTS AND DISCUSSION

The pKa'_1, pKa'_2 and pKa'_3 value[16] of the ligand L-cysteine are 1.71, 8.35 and 10.78 (Scheme 1) respectively at 25°C. Thus at pH 6.5 the ligand exists mainly as neutral molecule and the amount of protonated form will be less.

$$SH\text{-}CH_2CH(\overset{+}{N}H_3)\text{-}COOH \overset{pK_{a1}'}{\rightleftharpoons} SH\text{-}CH_2CH(\overset{+}{N}H_3)\text{-}COO^- + H^+ \quad (1)$$

$$pK_1' = 1.71$$

$$SH\text{-}CH_2CH(\overset{+}{N}H_3)\text{-}COO^- \overset{pK_{a2}'}{\rightleftharpoons} {}^-S\text{-}CH_2CH(\overset{+}{N}H_3)\text{-}COO^- + H^+ \quad (2)$$

$$pK_2' = 8.35$$

$${}^-S\text{-}CH_2CH(\overset{+}{N}H_3)\text{-}COO^- \overset{pK_{a3}'}{\rightleftharpoons} {}^-S\text{-}CH_2CH(NH_2)\text{-}COO^- + H^+ \quad (3)$$

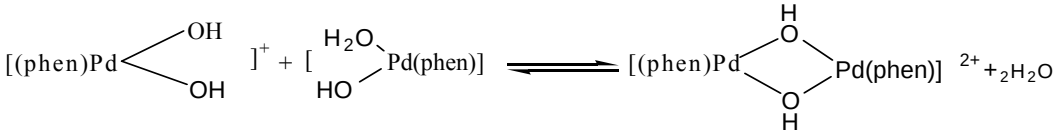
$$pK_3' = 10.78$$

Scheme 1

Again on the other hand the first acid dissociation equilibrium of the complex $[Pd(1,10\text{-phen})(OH_2)_2]^{2+}$ is

$$[Pd(1,10\text{-phen})(OH_2)_2]^{2+} \overset{pK_{a1}}{\rightleftharpoons} [Pd(1,10\text{-phen})(H_2O)(OH)]^+ + H^+ \quad (4)$$

The pK_1 value of the complex is determined by following the standard method [17] in laboratory and is found 6.05 at 25°C. At pH 6.5 the complex mainly exist as a μ-dihydroxobridged[13,18-20]species,$[Pd_2(1,10\text{-phen})_2(OH)_2]^{2+}$. The possibility of dimerisation of the complex may be as follows, because H_2O is good leaving group whereas OH is good nucleophile.



where phen= 1,10-phenanthroline

The complex starts to dimerised[19] at pH 4.0. The Job's method of continuous variation of the complex formation indicates a 2:1 metal-ligand ratio in the product complex. This is possible only when a bridge-substituted product is formed with the neutral species of L-cysteine through sulfur donor site[21, 22]. At constant pH 6.5 and fixed concentration of the complex (**1**) the $\ln(A_\infty - A_t)$ versus time 't' plot for different ligand concentration indicates a two steps process. Both are dependent on the incoming ligand concentration and limiting rate is not reached (Figure- 5) the rate constant for such process can be evaluated by assuming the following scheme.

$$(A) \overset{k_1}{\rightarrow} (B) \overset{k_2}{\rightarrow} (C)$$

Where A is the μ-dihydroxobis(1,10-phen)dipalladium(II) species, B is the intermediate with monodentate RSH (L-cysteine) and C is the final chelated sulfur bridged $[Pd_2(1,10\text{-phen})_2(OH)RSH]^{3+}$, where RSH =L-cysteine. Formation of C from B is predominant after some time has elapsed.

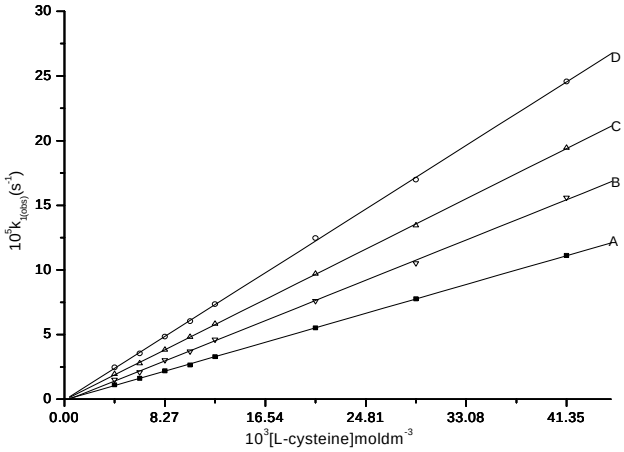


Fig.- 5. Plot of 10^3[L-cysteine] versus $10^5k_{1(obs)}$ at different temperatures
A = 20 ^{0}C, B = 25 ^{0}C, C = 30 ^{0}C and D = 35 ^{0}C

Calculation of k_1 for A → B

At a particular temperature the rate constants $k_{1(obs)}$ were found from the slope of the linear part of $\ln(A_\infty - A_t)$ versus time 't' plot, (Figure-3) for different ligand concentrations (when t is small). Due to steric hindrance of amino acid L-cysteine and poor leaving group property of OH^-, this associative path is slow and dependent of ligand concentration. For different temperature the $k_{1(obs)}$ values are obtained directly from the limiting slope and collected in Table 1. The second order rate constant of k_1 values for the first step are obtained from the Figure-6.

Table-1: $10^5k_{1(obs)}$ (s^{-1}) values at different [L-cysteine] and at different temperatures [complex(**1**)] = 4.135×10^{-4} mol dm^{-3}, pH= 6.5, ionic strength= 0.1 mol dm^{-3} $NaClO_4$.

10^5 [L-cysteine] (mol dm^{-3})	Temp(^{0}C)			
	20	25	30	35
4.135	4.81	5.43	6.11	6.72
6.20	7.24	7.86	9.20	10.35
8.270	9.64	10.72	12.44	13.54
10.34	11.92	13.55	15.24	16.78
12.40	14.96	16.22	18.44	20.83

Calculation of k_2 values for B → C step

The B → C step is ring closure through lone pair donation by the sulfur atom of the amino acid L-cysteine at the same time rapid elimination of bridged hydroxyl($^-$OH) group. After the completion of the reaction pH is quite increased, which support the evidence of hydroxyl group ($^-$OH) from the dipalladium bridged system. At particular temperature the slope of ln ($A_\infty - A_t$) versus time 't' plot for different L-cysteine concentration is found to be constant in the region, (Figure-7) the rate constant $k_{2\,(obs)}$ (Table-2) for B → C step can be evaluated from the method of Weyh and Hamm[15] using the consecutive rate law.

$(A_o - A_t) = a_1 \exp(-k_{1(obs)}\, t) + a_2 \exp(-k_{2(obs)}t)$
or $(A_o - A_t) - a_2 \exp(-k_{2(obs)}t) = a_1 \exp(-k_{1(obs)}\, t)$

Where a_1 & a_2 are constants depend on the rate constant and extinction coefficient. The value of $[(A_o - A_t) -- a_2 \exp(-k_{2(obs)}t)]$ are obtained from X- Y at different time t (Figure- 3). So $\Delta = a_1 \exp(-k_{1(obs)}\, t)$ or

$\ln\Delta$ = constant $k_{1(obs)}$- t. $k_{1(obs)}$ is derived from the slope of the $\ln\Delta$ versus t (where t is large) A similar method of calculation is followed for each ligand concentration in the range of 4.135 x 10^{-3} mol dm^{-3} to 12.40 x10^{-3} mol dm^{-3} at constant [Complex(**1**)] (4.135x10^{-4}) at pH 6.5, μ = 0.1 (M) $NaClO_4$ and at different temperatures e.g. 20, 25, 30 and 35 °C.

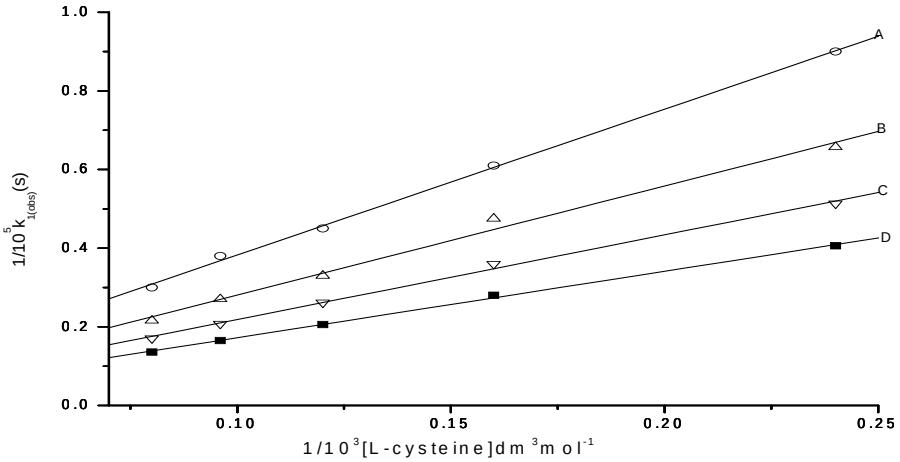


Fig.- 6. Plot of $1/10^3$[L-cysteine] versus $1/10^5 k_{1(obs)}$ at different temperatures
A = 20 ^{0}C, B = 25 ^{0}C, C = 30 ^{0}C and D = 35 ^{0}C

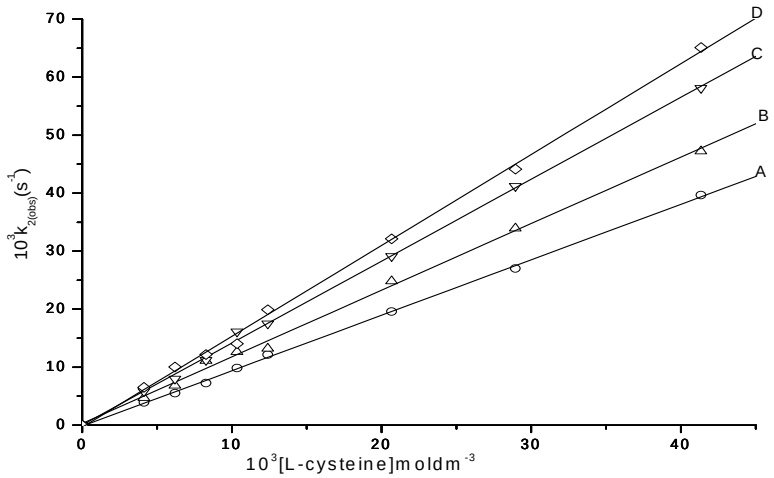
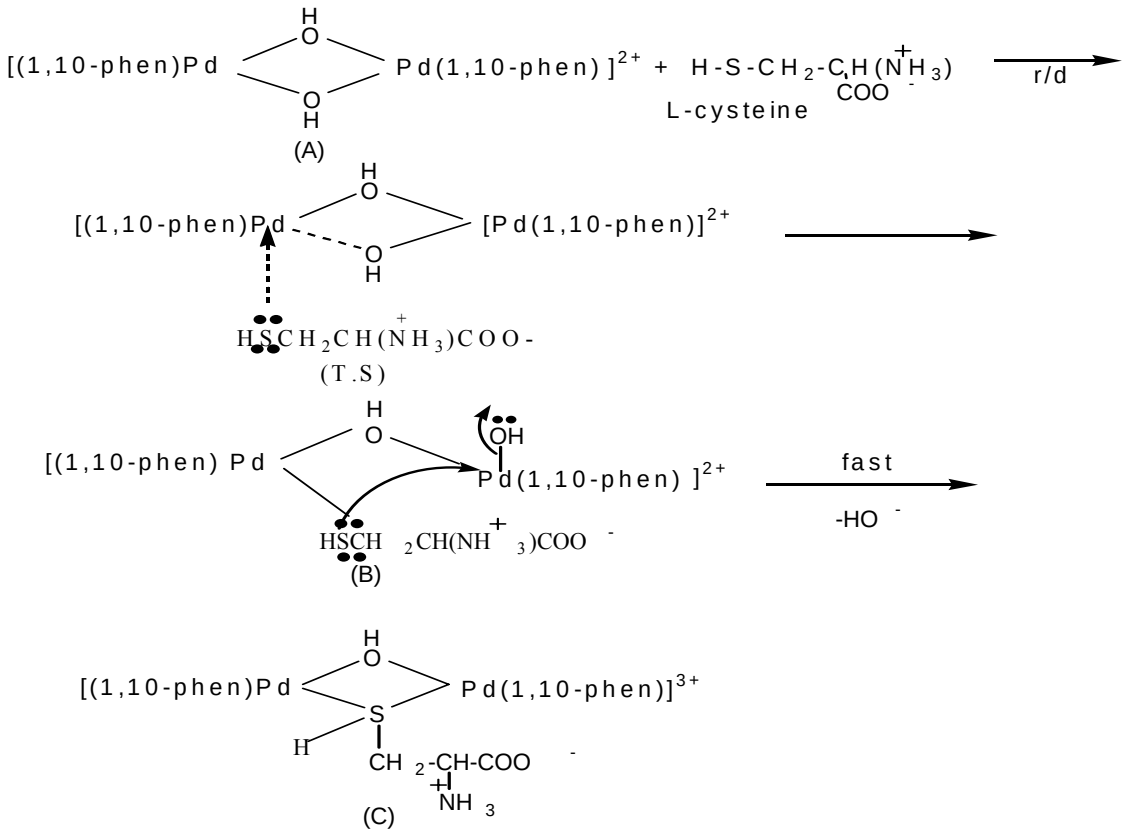


Fig.- 7. Plot of 10^3[L-cysteine] versus $10^3 k_{2(obs)}$ at different temperatures
A = 20 ^{0}C, B = 25 ^{0}C, C = 30 ^{0}C and D = 35 ^{0}C

The $k_{1(obs)}$ values thus obtained are linearly dependent on the studies concentration range . However, studies at further higher concentration up to 41.35x 10^{-3} mol dm^{-3} also follow the linearity (Figure-5). The ligand concentration dependence of $k_{1(obs)}$ can be explained by considering the following scheme 2 involving the formation of transition with increased co-ordination number. At pH 6.5 we may propose the mechanism of the interaction is as follows in Scheme 2.



Scheme 2

Table-2: $10^3 k_{2(obs)}$ (s^{-1}) values at different [L-cysteine] and at different temperatures [complex(**1**)] = 4.13×10^{-4} mol dm^{-3}, pH= 6.5, ionic strength= 0.1 mol dm^{-3} $NaClO_4$

10^3 [L-cysteine] (mol dm^{-3})	Temp(^{0}C)			
	20	25	30	35
4.135	3.91	4.72	5.86	6.52
6.20	5.52	6.86	8.01	10.01
8.270	7.25	11.11	11.23	12.18
10.34	9.86	12.61	14.06	16.13
12.40	12.14	13.20	17.51	19.92

However, the first order dependence of rate on [L-cysteine] may also fit with the other scheme involving the formation of an outer sphere associative transition step. We prefer the mechanism as described in the former scheme-2, because we could not obtained any evidence for the outersphere associative path. The second order rate constants (k_1 and k_2) are calculated from the slope of (Figure-6 & Figure-8) $k_{1(obs)}$ (s^{-1}) and $k_{2(obs)}$ (s^{-1})versus [L-cysteine] (mol dm^{-3}) respectively at different temperatures are collected in (Table- 3). However experimental result shows a similar curvature of $\ln(A_\infty - A_t)$ versus t plot at different temperatures for varying ligand concentration. The assumption of two consecutive steps for such a reaction and compulsion of k_1 and k_2 values fits properly with the experimental values.

Table-3: The second order rate constant k_1 and k_2 values

Temp (^{o}C)	$10^5 k_1$($dm^3 mol^{-1} s^{-1}$)	$10^3 k_2$($dm^3 mol^{-1} s^{-1}$)
20	41.66	20.11
25	50.12	28.14
30	62.55	66.66
35	83.33	100.12

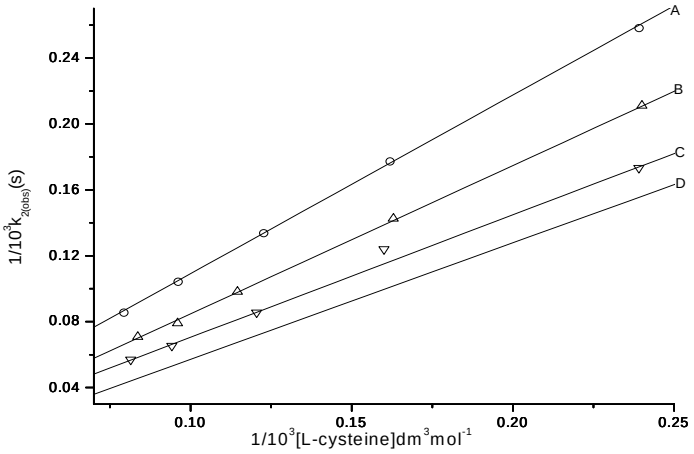


Fig.- 8. Plot of $1/10^3$[L-cysteine] versus $1/10^3 k_{2(obs)}$ at different temperatures
A = 20 ^{0}C, B = 25 ^{0}C, C = 30 ^{0}C and D = 35 ^{0}C.

Effect of change of pH on reaction rate

The kinetics of the reaction is studied at different pH values. The k_{obs} values are found to increase in pH in the studied pH ranges. Both the k_{obs} values are collected in Table 4. The enhancement in the rate of the reaction may be explained on the basis of the three equilibriums in the studied pH range (pH 5.5- 7.4) with increase in pH the percentage of diaqua species is reduced and percentage of the dimer hydroxo aqua palladium (II) species in solution increased. The hydroxo species is more reactive due to the well-known labialising effect of the -OH group via its π- bonding ability and strong electrometric effect. As a result the rate enhancement with increase in pH can be accounted. On the other hand the pKa_1, pKa_2 and pKa_3 values [16] of the ligand L-cysteine are 1.71, 8.35 and 10.78 respectively at 25 ^{0}C. At the pH 6.5 the amount of the protonated form will be less and neutral species will be present in appreciable amount. In this pH range, the amount of deprotonated form increases and the zwitter ionic form (LH) predominates which also partly account for the enhancement of the rate with increase in pH, in $10^5\, k_{1(obs)}$ values are 4.28, 4.81, 5.24 and 5.88 (s^{-1}), and $10^3\, k_{2(obs)}$ values are 3.42, 3.91, 5.24 and 5.86 (s^{-1}) at pH 5.5, 6.5, 7.0 and 7.4, respectively.

Effect of temperature on reaction rate

The reaction is studied at four different temperatures for different ligand concentration and the second order rate constant are summarised in Table 3. The activation parameters for both the steps (A)→ (B) and (B) → (C) are evaluated from the linear Eyring plots (Figure-9 & Figure-10) and compared with the literature data of the analogous systems [24-26] (Table 4). The low $\Delta H^{\neq}$ value, at the same time negative $\Delta S^{\ddagger}$ values, suggests ligand participation in the transition state for both the steps. The positive energy required for the bond breaking process is partly compensated, for the negative energy obtained from bond formation in the transition state and hence, low value of $\Delta H^{\ddagger}$ is observed. The participation of L-cysteine in the transition state result in more compact state than that of the initial reactant and negative entropy values are found.

Table- 4: Activation parameters for analogous systems

System	$\Delta H_1^{\ddagger}$ ($KJmol^{-1}$)	$\Delta S_1^{\ddagger}$ ($JKmol^{-1}$)	$\Delta H_2^{\ddagger}$ ($KJmol^{-1}$)	$\Delta S_2^{\ddagger}$ ($JK^{-}mol^{-1}$)	Reference
$[Pd_2(phen)_2(OH)_2]^{2+}$ /L-cysteine	75.22± 3.58	-98.94±4.67	68.81± 3.22	-110.27±5.26 ---	This Work
DL-penicillamine	45.39 ±1.4	-93.41± 2.3	---		23
$[Pd(Me_4dien)(OH)_2]^{2+}$/				-49.0	
Cl^-	---	---	40.0	-47.0	24
Br^-	---	---	39.0	-55.0	
I^-	---	---	34.0		
$[Pd(Et_4dien(OH)_2]^{2+}$/				-45.0	
Cl^-	---	---	56.0	-32.0	24
HCO_3^-	---	---	68.0		
$[Pd(OH_2)_4]^{2+}$ /				-44.0	
Me_2SO		---	58.0		25
Water exchange		---	49.0	-26.0	26

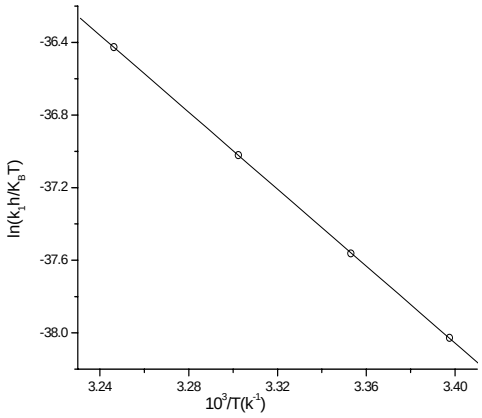


Fig.- 9: Eyring plot of ($\ln k_1 h/K_B T$ versus $10^3/T$)

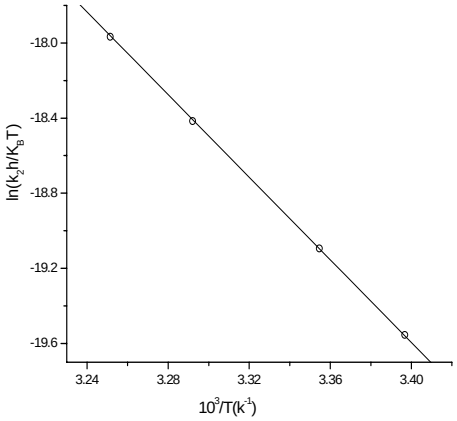


Fig.-10: Eyring plot of ($\ln k_2 h/K_B T$ versus $10^3/T$)

CONCLUSION

The interaction of L-cysteine with the titled palladium(II) complex proceed via two distinct consecutive substitution steps of bridged hydroxo (OH) group ($k_1 \approx 10^{-5} dm^3 mol^{-1} s^{-1}$ and $k_2 \approx 10^{-3}\ dm^3 mol^{-1} s^{-1}$). Each step proceeds via an associative activation pathway. The bonding mode of L-cysteinee to palladium(II) complex is not fully understood, but it is already noticed in I.R. Spectrum, $\upsilon Pd_{(II)\ -S}$ appear at $438cm^{-1}$ which fully supports the formation of sulfur coordinated bridging with the two Pd(II) centres [27]. Again the $[Pd_2(1,10\text{-phen})_2(OH)_2]^{2+}$ do not react to the azide (N_3^-), cytidine and glycine. It reacts to a good extend L-cysteine; DL-penicillamine, thioglycolic acid, DL-methionine and thiosemicarbazide all sulfur containing bio-molecules. It is also supported from the soft nature of Pd(II) towards the sulfur. Thus again it support that nitrogen is not a coordinate site of the bio molecules, for the ligand to behave as a bridging one with

the hydroxo bridged complex the mono atom Sulfur bridging is the best fitting among the other possibilities. After the completion of reaction, the pH of the solution increased which might be due to expulsion of the bridged –OH group, consequently ring closure occur through sulfur bridging[21,22] . A sharp peak at 472 cm^{-1} appears due to Pd(II)-S-Pd(II) stretching frequency[27],alike the Pt(II)-S-Pt(II) stretching frequency at 524cm^{-1}. The assumption of dimer formation of the starting complex may also be supported by the above fact, as the ligand remains neutral in this range. At higher pH (>6.0) the bridge opens and it forms hydroxy substituted complex[28-31]. At higher range of pH (>7.4) is not study due to formation of precipitate in the reaction cell during the kinetics studies. With an increase in pH the percentage of more reactive hydroxoaquapalladium(II) species in the solution is increased. The rate enhanced because hydroxo species is more reactive due to the well known labilsing effect of –OH group via its π- bonding ability and strong electromeric effect. The sulfur forms the associated transition state with the complex in the r/d step, followed by opening of the bridged –OH group from the Pd (II) and simultaneously ring closure occur through sulfur bridging via OH^- expulsion.

ACKNOWLEDGEMENTS

The authors SCM & GKG are thankful to National Institute of Technology, Durgapur- 713209 and Government of India for providing the necessary assistance and financial supports for carrying out this work.

REFERENCES

1. Kostova, **1**(1),1-22 (2006).
2. T. Rau and R. Van Eldik, *in Metal Ion in Biological System*, edited by A. Sigel ,Marcel Decker, New York, **32**, (1996).
3. *Cis-platin Chemistry & Biochemistry of a Leading Anticancer Drug*, edited by B. Lippert (Wiley-VCH, Zurich) (1999)
4. J. Reedjik, *Chem. Rev*. **99**, 2499 (1999).
5. E.R. Jamieson & S.J. Lippard, *Chem. Rev*., **99**, 2467 (1999).
6. L. Johnsson, M. Tilest, J.A.Habinger and J.E. Bercaw, *J.Am.Chem.Soc*. **122,**10846 (2000).
7. M.R. Plutino, L.M. Scolaro, R. Romeo and A. Grassi, *Inorg.Chem*. **39**, 2712(2000).
8. R. Romeo, M.R. Plutino, L.M. Scolaro, S. Stoccoro and G. Minghetti, *Inorg.Chem*. **39**, 4749 (2000).
9. D. Daganyi, A.Hofmann and R. Van Eldik, *Angew.Chem.Int.Ed*., **40**, 1680 (2001).
10. A. Shoukry, T. Rau, M. Shoukry and R. Van Eldik, *J.Chem. Soc., Dalton Trans*. **3105** (1998).
11. Z.D. Bugarics, G. Liehr and R.Van Eldik, *J.Chem.Soc. Dalton Trans*. **951**(2002).
12. A. Broomhead, D.P. Fairlie & M.W. Whitehouse, *Chem-Biol. Interact***, 31**, 113(1980).
13. S. Wimmer, P. Caston, F.L. Wimmer & N.P. Jhonson *J. Chem. Soc., Dalton Trans.* **403** (1989)
14. R.W. Hay & A.K. Basak, *J. Chem. Soc., Dalton Trans*. **1819** (1982).
15. J.A. Weyh & R.E. Hamm, *Inorg. Chem*. **8,** 2298 (1969).
16. R.M. Smith & A.E. Marttu, *Critical Stability Constants*, (Plenim Press, NewYork), P-21 (1989).
17. H. Hohmann & R.Van Eldik, *Inorg. Chim. Acta*, **174,** 87-92 (1990)
18. G. Alibrandi, M. Cusumano, A. Giannetto & D. Minnitti, *J. Chem. Soc., Dalton Trans.* 375 (1989).
19. El-Sherif A. Ahmed, M.Mohamed Shoukry & R. Van Eldik, *J. Chem. Soc.,Dalton Trans.* **1425** (2003).
20. A. Adrian Rafael, A. Broker Grand, R.T. Tiekink Edward, A. Walmsley Judith, *Inorg. Chim. Acta*, **361**, 1261 (2008).
21. L. Zhu & N.M. Kostic, Inorg. *Chem*. **31**, 3994 (1992).
22. L. Zhu & N.M. Kostic, *Inorg. Chim. Acta*, **21,** 217 (1994).
23. G.K. Ghosh, S.C. Moi & A.K. Patra, *Rasayan Journal of Chemistry*, **Vol.2**, No.3,724 (2009)
24. G. Mahal & Van Eldik R, *Inorg Chem.*, **24**, 4165 (1985).
25. Y. Dulommum, B. Hellquist, L.I. Elding& A.E. Merbach., *Inorg .Chem.,* **26**,1759 (1987).

26. L. Helm, L.I. Elding & A.E. Merbach, Helv *Chim Acta.* **67**, 1453 (1984).
27. P. S. Sengupta, R. Sinha & G.S. De, *Trans. Metal Chem*. **26,** 638 (2001).
28. M. Shoukry and R.Van Eldik, *J. Chem. Soc., Dalton Trans,* 2673 *(1996).*
29. T.M. Buslacva and A.S. Simanova**,** *Russ. J. Coord. Chem. Rev.,* **25**, 151 (1999).
30. P. Banerjee**,** *Coord. Chem. Rev.,* **19,** 192 (1999).
31. M. Ray, S. Bhattacharyya and P. Banerjee, *J. Indian Chem. Soc*., **76**, 151 (1999).

(Received: 6 November 2009 Accepted: 13 November 2009 RJC-481)