# RATE STUDIES ON THE SUBSTITUTION REACTIONS
# OF SQUARE PLANAR TETRAKIS(THIOUREA)PALLADIUM(II)
# CHLORIDE WITH SOME AMINO ACIDS

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The kinetics of the substitution reactions of square planar complex, $[PdL_4]Cl_2$ (L = thiourea) with some aminoacids such as glycine, DL-α-alanine, L-asparagine, DL-valine, DL-serine, L-proline and DL-threonine has been studied spectrophotometrically. The first order rate constant, $K$ was evaluated and linear plots were also obtained by plotting $K$ and [Y], the concentration of amino acid. The results indicate that the substitution reactions proceed by a displacement mechanism following the known two term rate law.

In recent years, the studies on the substitution reactions of square planar complexes mostly belonging to $d^8$ system, *e.g.* $Ni^{2+}$, $Pt^{2+}$ and $Pd^{2+}$ have been carried out by a large number of workers, specially those of Basolo and coworkers[1-6]. The substitution studies on $Pd^{2+}$ complexes[7] are largely carried out on amines complexes and effect of different entering groups have been studied, and is correlated with the *trans*-directing properties and nucleophilic reactivities of the ligands. From the literature it appears that no efforts have yet been made to study the role of amino acids as entering groups in the substitution reactions of square planar complexes. This is perhaps due to the paucity of informations regarding the order of nucleophilic reactivity and *trans*-directing orders of amino acids.

The present study on the kinetics of substitution reaction of tetrakis(thiourea)-palladium(II) chloride, $[PdL_4]Cl_2$ (where L is thiourea) with amino acids is the first step towards the studies of systems concerning with the kinetic investigations on the interaction of amino acids with square planar complexes in general.

## EXPERIMENTAL

All the amino acids used were biochemically pure B.D.H. products. The solutions of the reagents were prepared in doubly distilled air free water. $PdCl_2$ (Johnson & Matthey, London) was used for the preparation of complex.

### Preparation of Tetrakis(thiourea)palladium(II) Chloride

The mixture of 50 ml solution of 1% $PdCl_2$ in HCl and 5 g of solid thiourea was heated over a waterbath till all the thiourea was dissolved. Any insoluble residue left was filtered off, the filtrate was diluted by adding 50 ml of water and evaporated to one half of its volume. After

72 h, red crystals of the complex were separated, washed with acetone and dried in a desiccator over CaO. $C_4H_{16}N_8S_4PdCl_2$ (482·1) calculated: 9·9% C, 3·3% H, 23·1% N, 26·6% S; found: 10·1% C, 3·3% H, 23·2% N, 26·5% S. Spectrophotometric measurements were carried out by using a Bausch and Lomb Spectronic 20 spectrophotometer and 1 cm cuvettes. The $\lambda_{max}$ of $[PdL_4]Cl_2$ was observed at 360 nm. With amino acids, the selected temperature was 575 nm, where thiourea complex and amino-acid complex have vast difference in absorbancies, the latter absorbing more strongly. The absorbancies of the amino-acids complex ($A$) were obtained by keeping the mixture over night and measuring the absorption until reasonably constant values were obtained. All the measurements were carried out at constant temperature by dipping the solution in a thermostat (type N.B.E. Germany) with a sensitivity of $\pm 0.5°C$. The first order rate[7] was determined by plotting $\log (A - A_0)/(A - A_t)$ vs time $t$ and the rate constant $K$ is given by the expression

$$K = (2·303/t) \log/(A - A_0)/(A - A_t),\qquad(1)$$

where $K$ is observed first order constant, $A$ the maximum absorbance value, $A_t$ the absorbance value at time $t$, $A_0$ the initial absorbance value. Values of rate constant were calculated from the slope of the linear rate plots.

TABLE I

Rates of Reaction of Square Planar $[Pd L_4]Cl_2$ Complex with Various Amino Acids in Aqueous Solutions

35°C, pH $\approx$ 6·5 $[PdL_4Cl_2] = 1 . 10^{-3}$M, $I$ 0·10.

| Amino acid concentr., M | $K$, min$^{-1}$ . $10^{-3}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | A[a] | B | C | D | E | F | G |
| 1·0 . $10^{-1}$ | 8·62 | 3·03 | 4·10 | 2·99 | 4·88 | 3·63 | 5·75 |
| 5·0 . $10^{-2}$ | 5·29 | 3·45 | 3·08 | 3·17 | 4·09 | 3·86 | 5·75 |
| 3·3 . $10^{-2}$ | 5·02 | 3·45 | 3·05 | 4·16 | 3·82 | 4·14 | 5·29 |
| 2·5 . $10^{-2}$ | 4·48 | 3·31 | 5·47 | 7·59 | 3·48 | 6·21 | 5·75 |
| 2·0 . $10^{-2}$ | 5·29 | 6·67 | 5·32 | 9·25 | 5·11 | 4·21 | 6·44 |

[a] A glycine, B DL-α-alanine, C L-proline, D L-asparagine, E DL-serine, F DL-threonine, G DL-valine.

## RESULTS AND DISCUSSION

The substitution reactions of square planar $[PdL_4]Cl_2$ have been studied by spectrophotometric measurements taking advantage of the fact that intense colour is developed on the addition of amino acid in $[PdL_4]Cl_2$ solution. Moreover, the absorption of the latter is significant in comparison to the absorption of the complex solution containing amino acids at a selected wave length (575 nm). In general, the kinetic data on the substitution reactions of square planar complexes can be represented in terms of a bimolecular displacement mechanism, following a two term rate law[8]:

$$\text{Rate} = k_1[\text{PdL}_4\text{Cl}_2] + k_2[\text{PdL}_4\text{Cl}_2]\,[\text{Y}]$$

for the general reaction, where [Y] is the proper amino acid. The mechanism can be written as

$$[\text{PdL}_4]^{2+} + [\text{Y}] \rightarrow [\text{PdL}_3\text{Y}]^{2+} + \text{L},$$

where $k_1$ and $k_2$ are the first and second order rates respectively. The experimental first order rate constant $K$ is related to $k_1$ and $k_2$ by the relation: $K = k_1 + k_2[\text{Y}]$. Following Basolo[7], the rate constant $k_1$ represents the slow displacement of thiourea by the solvent ($\text{H}_2\text{O}$), which then is readily replaced by amino acid.

A direct nucleophilic displacement of thiourea by amino acid is responsible for $k_2$. The path mechanism for the substitution by amino acid $\big[\text{Y}\big]$ in such a system has been represented by the following scheme:
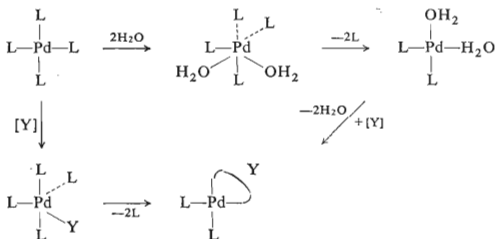


Applying the two term rate law on the substitution reactions of $\text{Pd}^{2+}$, the plots of $K$ *vs* [Y] for the various amino acids indicate a linear relationship in case of glycine, L-asparagine, L-proline, DL-serine and DL-α-alanine. However, no such relationship exists in DL-valine and DL-threonine. The values of $K$, $k_1$, and $k_2$ are given in Table I. The values of $k_1$ (min $10^{-3}$) and $k_2$ (mol$^{-1}$ min $10^{-2}$) for the amino acids used are: glycine 4·10, 0·576, DL-α-alanine 3·50, 1·66, L-p oline 3·0, 2·12, L-asparagine 8·70, 7·5, DL-serine 4·80, 3·30, DL-threonine 3·15, 2·00. The $K$ values for the various amino acids follow the order: glycine > DL-valine > DL-serine > L-proline > DL-threonine > DL-α-alanine > L-asparagine which roughly corresponds to the order of increasing ionization constants of α-amino carboxylic group[9]: DL-alanine > glycine > > DL-valine > DL-serine > DL-threonine > L-asparagine > L-proline. Only DL-α-alanine and L-proline deviate from the above order. This indicates the influence of ionization on the extent of substitution of amino acid in the complex. The plot of $K$ *vs* ionization constant for various amino acids indicate a linear relationship for glycine, DL-valine, DL-serine, DL-threonine and L-asparagine belonging to mono-aminodicarboxylic class deviates appreciably from the linear relationship, apparently

du$\varepsilon$ to lower ionization constant. The plot of $K$ $vs$ $pK_a$ indicates a linear relationship in case of DL-valine, DL-serine, DL-threonine and L-asparagine. Deviation is observed in case of glycine, DL-$\alpha$-alanine and L-proline. The departure from linearity in case of glycine is due to the low $pK_a$ value of glycine in comparison to its analogues[10] $e.g.$, DL-valine, DL-serine and DL-threonine, where a consistent decrease in $pK_a$ is observed. The fact that nucleophilic character is somewhat dependent on $pK_a$ values can be demonstrated in these studies, where $K$ increases with $pK_a$ in case of four amino acids, DL-valine, DL-serine, DL-threonine and L-asparagine.

As mentioned above the dependence of $[Y]$ on $K$ followed a linear relationship in case of L-asparagine, glycine, L-proline, DL-valine, DL-$\alpha$-alanine and DL-serine and with $k_1 < k_2$, however, in DL-valine and DL-threonine the rate law does not hold good. There is no satisfactory explanation for this anomaly, but such types of reactions are well characterized and proceed only with a solvent assisted dissociation mechanism. The value of the formation constant for the general reaction,

$$[PdL_4]^{2+} + n[Y] \xrightleftharpoons{-K_f} [PdL_4(Y)_n]^{2+}$$
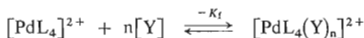
can be calculated by the spectrophotometric method[11] on following the expression,

$$\log A_a - A_0/A - A_a = \log K_f + n \log [Y^-],$$

where $A_a$, $A_0$ and $A$ are the absorbances of the complex on addition of ligand $[Y]$ at time $t$, without addition of the ligand and at completion of the reaction respectively. The plot of $\log A_a - A_0/A - A_a$ $vs$ $\log [Y]$ is found to be linear and values of $n$ and $\log K_f$ were computed from the slope and intercept, respectively.

The values of $\log K_f$, $n$ and $pK_a$ for the amino acids used are: L-asparagine 0·880, 1·1, 8·85, glycine 1·408, 1·1, 9·86, L-proline 2·070, 1·7, 10·68. The dependence of $\log K_f$ on $pK_a$ is found to be linear for proline, glycine and DL-valine, L-asparagine deviates from the linearity. Such type of plot is similar to that given by Bjerrum[12] for various ligands of the same type interacting with a particular metal, and following the expression $\log K_f = \alpha pK_a + C$ where $\alpha$ and $C$ are constants. In the present case the values of $\alpha$ and $C$ are found to be 1·5 and $-13·90$, respectively.

From the present studies it may be concluded that amino acids in general, are potential ligands for substitution in Pd(II) square planar complexes. The system studied is first of its kind and indicates the vast field open for working on the substitution reactions of amino acids with square planar complexes.

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