

Inorganic Chemistry

KINETICS OF THE SUBSTITUTION REACTIONS OF SQUARE PLANAR COMPLEX, Pd(THIOUREA)₄Cl₂ WITH HETEROCYCLIC AMINES

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The kinetic studies on the substitution reactions of square planar metal complexes have been an area of extensive research for the last two decades. The main bulk of the recent work has been limited to Ni(II) group metals, namely Ni, Pd and Pt by Basolo *et al.* (1960, 1961), Malik (1972), Bekker and Robb (1975), and Coe and Rispoli (1976). Interesting correlations have been put forward between reactivities of the replaceable ligands and the rate of reactions. The mechanism of the substitution reactions has been explained on the basis of a two term rate law. The mechanism of the substitution reactions involving amino acids in the square planar complex, [Pd(tu)₄]Cl₂ (tu = Thiourea) has been reported by Farooq and Malik (1972).

The work described in this communication deals with the kinetic studies on the interaction of heterocyclic amines with tetrakis thiourea palladium(II) chloride using spectrophotometric and potentiometric methods of analysis.

Keywords: Palladium (II); Thiourea; Amines; Kinetics of Substitutions of Thiourea by Amines.

EXPERIMENTAL

Reagents

Palladium chloride (Johnson Matthey product) was used for the preparation of the thiourea complex. Thiourea (tu), o-phenanthroline (o-phen) and 2,2' dipyridyl (dipy) were analytical grade products. 2-,3- and 4-picolines, 2,4- and 2,6-lutidines were reagent grade chemicals and were further purified by distillation. The aqueous solutions of the amines were standardized by pH metric titrations against standard nitric acid using calomel and glass electrodes.

The preparation of tetrakis thiourea palladium(II) chloride has been described previously.

The spectrophotometric and potentiometric measurements were carried out using Bausch and Lomb Spectronic '20' colorimeter and 'Kaycee' potentiometer respectively.

In all the experiments, a constant ionic strength of 0.1M was maintained using KCl solution. The pH of the reactant mixture was kept at 6.5-7.0 using sodium acetate-acetic acid buffers.

KINETIC MEASUREMENTS

(i) Spectrophotometric Methods

The λ max. of the complex, [Pd(tu)₄]Cl₂ was observed at 360 m μ . For the systems [Pd(tu)₄]Cl₂ + L (where L is a heterocyclic amine), the selection of the

wave length was made at 600 m μ . All spectrophotometric measurements were made in a manner similar to that described previously for [Pd(tu)₄]Cl₂-amino acid systems by Farooq and Malik (1972). The plot of

$$\log \frac{[(OD)_\infty - (OD)_0]}{[(OD)_\infty - (OD)_t]} \text{ vs.}$$

time t , gives a straight line (Fig. 1). For 2,4- and 2,6-lutidines, it was found that precipitates formed almost immediately after achieving maximum absorbance. The k_{obs} values are summarised in Table I and II.

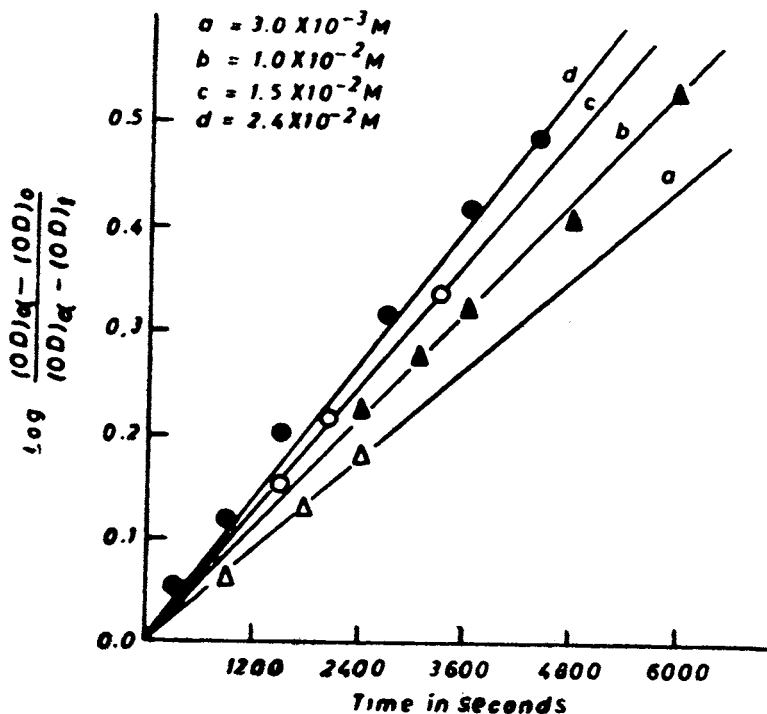


FIG. 1. Concn. of Pd (tu)₄Cl₂ = 1.0 × 10⁻³ M.

TABLE I

Values of k_{obs} at various pyridine concentrations (in presence of 0.1M KCl)

| Temperature °C | Concn. of the complex [Pd(tu) ₄]Cl ₂ in M | Concn. of py in M | $k_{obs} \times 10^{-5} s^{-1}$ |
|-------------------|--|------------------------|---------------------------------|
| 20 | 1 × 10 ⁻³ | 1.0 × 10 ⁻² | 3.6 |
| " | " | 1.6 × 10 ⁻² | 4.1 |
| " | " | 2.1 × 10 ⁻² | 4.8 |
| 25 | " | 3.0 × 10 ⁻³ | 3.2 |
| " | " | 1.0 × 10 ⁻² | 3.9 |
| " | " | 1.5 × 10 ⁻² | 4.3 |
| " | " | 2.4 × 10 ⁻² | 5.1 |

TABLE II
Values of k_{obs} for picolines and lutidines (in presence of 0.1M KCl)

| Temperature °C | Concn. of the complex [Pd(tu) ₄]Cl ₂ in M | Concn. of Amine in M | $k_{\text{obs}} \times 10^{-5} \text{ s}^{-1}$ |
|-------------------|--|--|--|
| 25 | 1.0×10^{-3} | 1.0×10^{-2} (2-picoline) | 6.2 |
| " | " | 1.0×10^{-2} (3-picoline) | 1.4 |
| " | " | 1.0×10^{-2} (4-picoline) | 1.7 |
| " | " | 1.0×10^{-2} (2,4-lutidine) | 3.4 |
| " | " | 1.0×10^{-2} (2,6-lutidine) | 4.0 |

(ii) *Potentiometric Method*

The kinetics of the substitution reactions involving tetrakis thiourea palladium(II) chloride and heterocyclic amines were also studied potentiometrically. The theoretical aspects and experimental verifications of this method have been discussed while reporting the kinetics of the interaction of heterocyclic amines with tris thiourea copper(I) iodide (Malik & Khan, 1971). In brief, the potentiometric method is based upon the fact that there could exist a linear relationship between the concentration of thiourea and e.m.f. using Ag-Ag₂S as an indicator electrode in the pH range of 5-8. Taking advantage of this characteristic of Ag-Ag₂S electrode reported by Malik and Khan (1971), the first order rate reaction was determined by plotting $\log \frac{E_t}{E_{\infty} - E_t}$ vs. t , where E_{∞} and E_t are the e.m.f. values at equilibrium and at time t respectively (Malik & Khan, 1973). The method was applied to the systems [Pd(tu)₄]Cl₂ + Py, [Pd(tu)₄]Cl₂ + picoline, [Pd(tu)₄]Cl₂ + dipy. and [Pd(tu)₄]Cl₂ + o-phen.

The plots of $\log \frac{E_t}{E_{\infty} - E_t}$ vs. t were found to be linear (Fig. 2), the k_{obs} values which are summarized in Tables I and II were obtained by multiplying 2.3 times the slope of the linear plots

$$k_{\text{obs}} = \frac{2.3}{t} \log \frac{E_t}{E_{\infty} - E_t}$$

RESULTS AND DISCUSSION

The kinetics of the substitution reactions of tetrakis (thiourea) palladium(II) chloride with pyridine, picoline, o-phenanthroline and dipyridyl were studied by spectrophotometric and potentiometric methods.

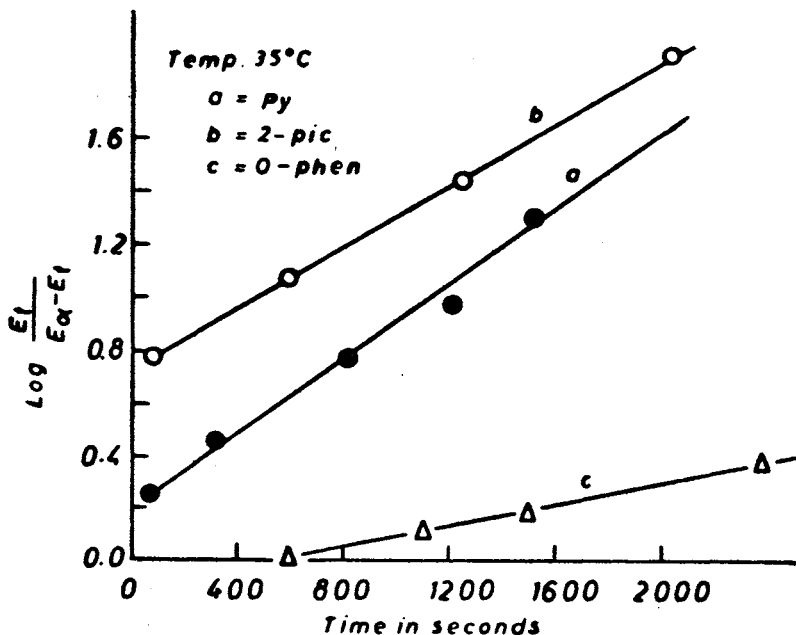


FIG. 2. Concentration of amine = 2.5×10^{-3} M.

The results of kinetic studies can be described by the equation (Basolo *et al.*, 1961; and Malik & Khan, 1971)

$$k_{obs} = k_1 + k_2 [Y] \quad \dots(1)$$

Equation (1) is equivalent to general rate law equation for ligand substitution in square planar metal complexes

$$\text{Rate} = k_1 + k_2 [Y] [\text{Complex}]$$

where k_1 and k_2 are first and second order constants respectively and Y is the entering group.

The equation (1) is valid for the present reaction study e.g., reaction of $[\text{Pd}(\text{tu})_4]\text{Cl}_2$ with pyridine and related compounds. The reaction involves the displacement of one or more thiourea molecules in the complex, $[\text{Pd}(\text{tu})_4]\text{Cl}_2$ by heterocyclic amine molecule. The values of k_{obs} are given in Tables I and II for pyridine, 2-, 3- and 4-picolines and lutidines. The values of k_{obs} vs. Y plotted for heterocyclic amines at 35°C are given in Fig. 3. The plots are straight lines with slopes equal to k_2 and intercept equal to k_1 .

The two term rate law applicable in this case requires a two step mechanism which has been proposed for ligand substitution in square planar complexes by Basolo and Pearson (1968).

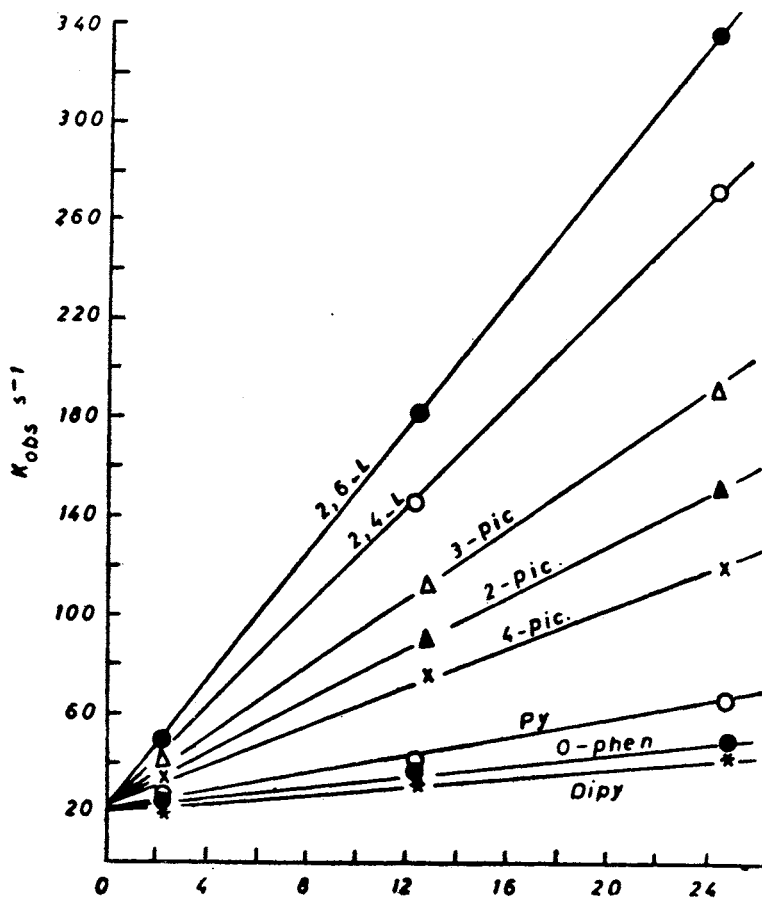
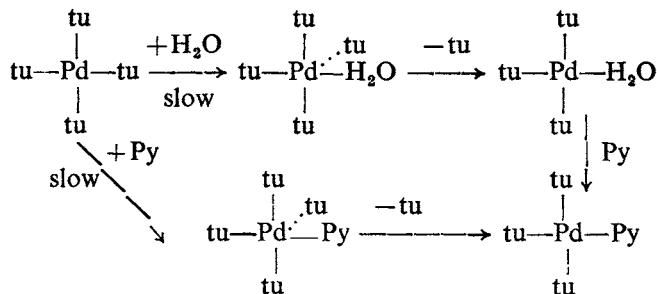


FIG. 3. Concentration of amine 1×10^{-3} M.



The rate constant k_1 is responsible for slow displacement of thiourea by water which is then readily replaced by pyridine where k_2 is simply a direct bimolecular SN_2 reaction between the incoming ligand pyridine and the complex, $[\text{Pd}(\text{tu})_4]\text{Cl}_2$. The effectiveness of pyridine as an incoming ligand is explained on the basis of

TABLE III

Comparison of rate of reactions of Pd(tu)₄Cl₂ with various heterocyclic amines in aqueous solution at 25 and 35 °C (in presence of 0.1M KCl)

| Temperature °C | Concn. of the complex [Pd(tu) ₄]Cl ₂ in M | Concn. of Amine in M | $k_{\text{obs}} \times 10^{-5} \text{ s}^{-1}$ |
|-------------------|--|--|--|
| 25 | 1.0×10^{-3} | 1.0×10^{-2} (py) | 4.2 |
| " | " | 1.0×10^{-2} (2-pic) | 6.4 |
| " | " | 1.0×10^{-2} (3-pic) | 1.3 |
| " | " | 1.0×10^{-2} (4-pic) | 1.5 |
| " | " | 1.0×10^{-2} (2,4-lutidine) | 3.2 |
| " | " | 1.0×10^{-2} (2,6-lutidine) | 4.2 |
| 35 | 5×10^{-4} | 2.5×10^{-3} (py) | 28.0 |
| " | " | 1.25×10^{-2} (py) | 39.0 |
| " | " | 2.5×10^{-3} (py) | 67.0 |
| " | " | 2.5×10^{-3} (2-pic) | 40.6 |
| " | " | 1.25×10^{-2} (2-pic) | 88.0 |
| " | " | 2.5×10^{-3} (2-pic) | 151.0 |
| " | " | 2.5×10^{-3} (3-pic) | 43.0 |
| " | " | 1.25×10^{-2} (3-pic) | 113.0 |
| " | " | 2.5×10^{-3} (3-pic) | 190.0 |
| " | " | 2.5×10^{-3} (4-pic) | 34.0 |
| " | " | 1.25×10^{-2} (4-pic) | 71.2 |

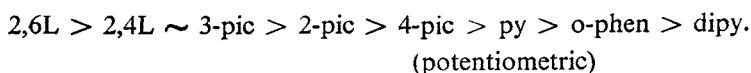
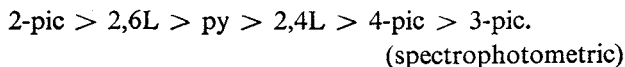
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TABLE III (contd.)

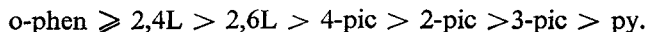
| Temperature °C | Concn. of the complex [Pd(tu) ₄] Cl ₂ in M | Concn. of Amine in M | $k_{\text{obs}} \times 10^{-5} \text{ s}^{-1}$ |
|-------------------|---|------------------------------------|--|
| " | " | 2.5×10^{-2} (4-pic) | 19.0 |
| " | " | 2.5×10^{-3} (2,4-L) | 43.0 |
| " | " | 1.25×10^{-2} (2,4-L) | 146.0 |
| " | " | 2.5×10^{-2} (2,4-L) | 268.0 |
| " | " | 2.5×10^{-3} (2,6-L) | 50.0 |
| " | " | 1.25×10^{-2} (2,6-L) | 181.0 |
| " | " | 2.5×10^{-2} (2,6-L) | 340.0 |
| " | " | 2.5×10^{-3} (dipy) | 21.7 |
| " | " | 1.25×10^{-2} (dipy) | 33.2 |
| " | " | 2.50×10^{-2} (dipy) | 41.80 |
| " | " | 2.5×10^{-3} (o-phen.) | 22.70 |
| " | " | 1.25×10^{-2} (o-phen.) | 37.20 |
| " | " | 2.50×10^{-2} (o-phen.) | 43.5 |

$d_{\pi} - p_{\pi}$ bond formation with the metal and thus stabilising the transition state by the formation of π -bond using $4d$ electrons of Pd(II).

A comparison of the k_{obs} values for the system : [Pd(tu)₄]Cl₂ + Amine (*vide* Tables I, II and III) evaluated from spectrophotometric as well as potentiometric methods reveals the following order for the various heterocyclic amines :



It is not possible to correlate the k_{obs} values with those of the pK 's of the substituent ligands, which follow the following order (Klinsberg, 1961)



However, it must be emphasised that basicity would be of little importance in such reactions and polarizability plays a determined role in the activity of nucleophile (Belluco *et al.*, 1965). On the basis of present studies, it is also not possible to make a quantitative correlation between k_{obs} values and nucleophilic reactivities, however, in alkyl pyridines under study, the nucleophiles are reported to be almost of the same order.

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