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KINETIC STUDY OF THE COMPLEXATION OF PALLADIUM (II) WITH 2-(5- BROMO -2- PYRIDYLAZO) -5- DIETHYLAMINOPHENOL

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ملخـــص

لقد تمت دراسة كيناتيكية التفاعل بين عنصر الباليديوم والمركب العضوي ٢ - (٥ - برومو - ٢ - بيريديل أزو) - ٥ - ثنائي أثيل امينو فينول في محلول ذو رقم هيدروجيني يساوي ٣,٥٣ وفي وجود ٥٠ ٪ ايثانول . واتضح أن رتبة التفاعل هي واحد لكل من العنصر والمركب العضوي . كذلك تمت دراسة تأثير القوة الايونية ودرجة الحرارة على معدل التفاعل . لقد تم اقتراح ميكانيكية التفاعل وكذلك حساب ثوابت ارهينوس وبعض الثوابت الحرارية الاخرى .

ABSTRACT

The kinetics of the complexation reaction of palladium with 2- (5- bromo -2- pyridylazo)- 5 - diethylaminophenol (5-Br-PADAP) has been studied in the stability time at the optimum pH of 3.53 in presence of 50% ethanol. The effect of ionic strength and temperature on the reaction rate were reported. A mechanism has been postulated and the stability constants of the individual steps were determined . The Arrhenius and thermodynamic parameters were evaluated and discussed .

INTRODUCTION

The reagent of 2 – (5– bromo –2– pyridylazo)–5–diethylaminophenol (5–Br–PADAP) has been used recently for the spectrophotometric determination of many metals. A review of the spectrophotometric cnaracteristics and analytical applications of this reagent has been given by Wei et al [1] . In general the spectrophotometric determinations of pd(II) suffer from the disadvantage of interference from the other platinum group especially Pt(VI) and Au (III) [2–9]. On the other hand, we find that the 5–Br–PADAP reagent is very selective for spectrophotometric determination of Pd (II) where Pt (VI) and Au (III) ions do not interfere at the optimum pH of 3.53 and at 590 nm[10] . Virtually no kinetic study is reported concering this reagent and its complexation with metals.

Therefore the present work represents the kinetic and the mechanism studies of the formation of the Pd(II)–5–Br–PADAP complex.

EXPERIMENTAL

Materials

All solutions were prepared from Analar grade reagents.
A stock solution of 10^{-2}M 5–Br–PADAP (Merck) was prepared by dissolving the appropriate amount in pure ethanol . A 10^{-2}M Pd (II) solution was prepared by dissolving the proper amount of palladium chloride in bidistilled water. Ionic strength was varied by adding pure KNO_3 . The acetic acid–sodium acetate buffer mixture (PH 3.35) was used .

Apparatus :

A pye–Unicam sp8 –100spectrophotometer equipped with kinetic facilities was used for the rate study and for recording spectra .
A corning pH- meter model 12 was used for pH measurements

Rate Measurements :

Kinetic measurements were undertaken in the stability time for full color development and at optimum pH of 3.53 where the violet complex showed maximum absorbance at 590 nm .

The concentration of Pd (II) used in the kinetic study was chosen in the linear portion of the Beer's law plot where absorbance was proportional to concentration . Kinetic runs were followed at ten seconds time intervals .

A least square computer programme was used for the analysis . The reported rate constant is the mean for four replicate runs . Activation parameters were obtained from Arrhenius plot and the appropriate transition state theory

Kinetic Procedure :

5.0×10^{-5} M solution of the metal and 1.0×10^{-4} M solution of the ligand in presence of 50% (V/V) ethanol at pH 3.53 were mixed . Before starting the reaction , all reactants were thermostated at the required temperature . The course of the reaction was followed by measuring the absorbance of the product complex at 590 nm.

RESULTS AND DISCUSSION

The absorbance – wavelength curves for the formation of the complex at different time intervals in shown in figure 1. It is evident that the absorbance increases with time thus enabling the reaction to be monitored . On the other hand , it is apparent that the maximum absorption of the complex is at 590 nm where there is no interference from the ligand which had its maximum absorption at 445 nm .

Rate constants

The analytical properties of the complex [10]showed that the molar ratio of pd(II) to 5 – Br–PADAP is 1:2. This is represented in the following equation

$$M + 2L \longrightarrow ML_2.$$

The above reaction is second order if its velocity is proportional to the product of concentrations of the two reactants metal and ligand .

The rate law for this system in differential from is

$$\frac{dx}{dt} = k(a - x)\ (2a - 2x)$$

where a is the initial concentration of the metal (5×10^{-5} M) , 2a is the initial concentration of the ligand (1.0×10^{-4} M) and x is the decrease in the concentration . The integrated form of above rate law will then be :

$$kt = \frac{x}{2a(a-x)}$$

Here x is proportional to the absorbance A_t of the complex at time (t)

and a is proportional to the absorbance at time infinity A_∞

Equation (2) above could then be rearranged to yield

$$\frac{A_t}{A\infty - A_t} = 2akt$$

Where a plot of $\frac{A_t}{A\infty - A_t}$ against time would give a straight line passing through the origin and having a slope of 2 ak thus the second order rate constant for the complexation reaction could be determined .

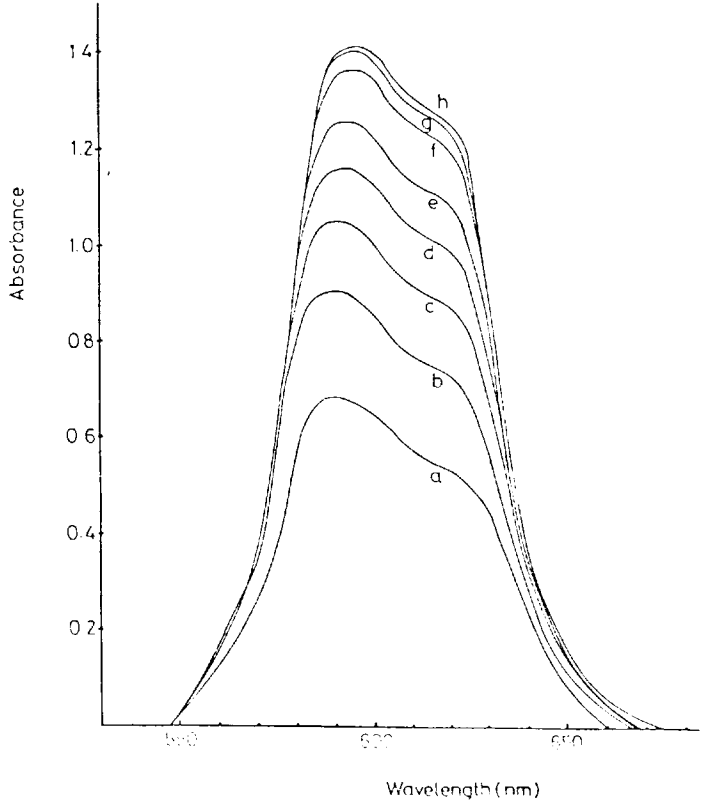


Fig . 1 . Absorbance – Wavelength curves for the complexation of Pd (II) with 5–Br–PADAP ([M] = 5 x 10^{-5} M) , ([L] = 1 x 10^{-4}) at pH 3.53 in 50% ethanol at various time intervals (min) : a, 3;b,6.5;c, 9.5; d, 13.5; e, 18.5; f, 27.5; g, 35; h, 24 hr.

The results of such plots are manifested in Figure 2 at five different temperatures . The Arrhenius plot is linear in the range (16 - 36° C) . The kinetic and thermodynamic parameters are presented in Table 1 .

Effect of Ionic Strength

There was no dramatic change in the rate constant when the ionic strength was varied by adding KNO_3 . The result is manifested in Table 2 .

Table 1 .

Specific rate constant , activation energy and thermodynamic Parameters of activation for the complexation reaction of Pd (II) with 5 – Br – PADAP at pH 3.53 in presence of 50% ethanol at 25°C

k/dm^3.mol^{-1}s^{-1}.	Ea≠/KJ mol^{-1}	△G≠/KJ mol^{-1}	△H≠/KJ mol^{-1}	△S≠./JK^{-1}mol^{-1}.
50.38 ± 0.02	55.12 ± 0.070	63.28	52.64	35.69

Table 2

Effect of ionic strength on the rate of the complexation reaction of Pd (II) with 5 – Br – PADAP at pH 3.53 in presence of 50% ethanol at 25°C .

k / dm^3.mol^{-1} s^{-1}.	Ionic Strength , μ
50.38	0.1
51.04	0.2
50.25	0.3
50.74	0.4

Reaction Mechanism :

From the above results , and since the stoichiometry of the reaction is 1 : 2 the following mechanism is postulated

$$L + M \xrightarrow{\text{slow}} ML \qquad \text{(rate – determining step)}$$

$$ML + L \xrightarrow{\text{fast}} ML_2 \qquad \text{where M = metal , L = ligand}$$

The results of the effect of ionic strength showed that , the rate–determining step did not involve similar or opposite charges but as proposed above where a charged species attacking a neutral molecule led to a negative salt effect. On the other hand , the results presented in Table 1 proved that the entropy of activation is negative , suggesting that the activated complex is formed by an association of the reactant molecules in the slow step. This is quite logical because the two independent molecules lose some translational and rotational freedom when the complex is formed .

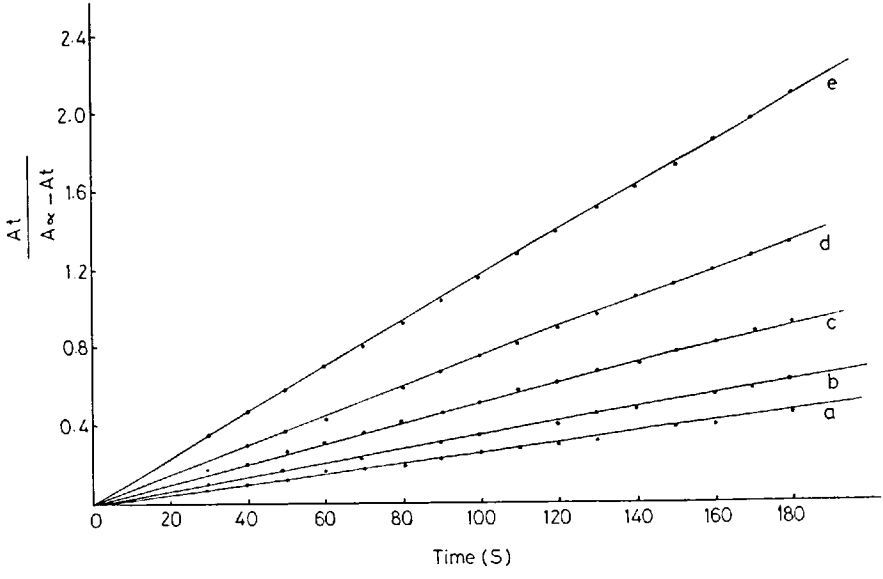


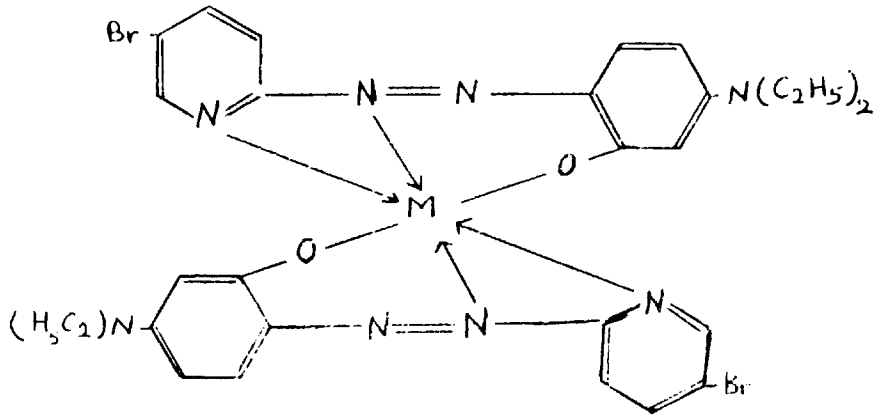
Fig. 2. Second order plots of $\frac{A_t}{A\infty - A_t}$ against time for the complexation reaction of Pd (II) with 5–Br PADAPat PH 3.53 in 50% ethanol at various temperatures a , 160 ° C ; b, 20°C; c, 2 5°C; d, 31°C; e, 36°C .

From the results of the molar ratio [10], the value of the apparent stability constant (log B) was found to be 11.47. The relationship between the overall stability constant and the individual ones in the above mechanism is

$$B = K_1 K_2 .$$
$$B = K^{\neq} K_2 .$$

$K^{\neq}$ was calculated from the transition state theory equation to be 8.09×10^{-12}. This would lead to a stability constant log K_2 of 22.56. Therefore, the product occuring in the slow step is so unstable that it forms instantaneously the final complex in a fast step with a considerable equilibrium constant .

. It is believed from the above results that the ligand 5 – Br– PADAP forms 1:2 type of complex with the following mode of bonding with Pd (II) ions .



where it is observed that the ligand behaved as a tridentate coordinating via the nitrogen atom of each azo group and of the pyridine ring and a covalent linkage with the oxygen of the hydroxyl group is formed . This is in accordance with the results obtained by comparing the I.R. spectra of ligand and complex [10].

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