



KINETIC DETERMINATION OF MICRO AMOUNT OF Pd(II)

T.G. Pecev, R.P. Igov, G.Ž. Miletić, M.N. Miljković

Faculty of Philosophy, Department of Chemistry, Ćirila i Metodija 2, 18000 Niš, Yugoslavia

Abstract: A new catalytic reaction is proposed and kinetic method developed for the determination of micro amounts of Pd(II) on the basis of its catalytic activity in oxidation of the indigo carmine by hydrogen peroxide in acetate buffer. The sensitivity of the method is $0.4 \mu\text{g}/\text{cm}^3$. The error is below 16% and the method has relatively good selectivity.

1. Introduction

Several kinetic method based on catalysed reactions have been used for determination of traces of Pd(II) [1-6].

In this paper, a new catalysed reaction is proposed and a kinetic method for the determination of trace amounts of Pd(II) in solution is described. The oxidation of the indigo carmine (IK) with hydrogen peroxide in the presence of acetate buffer gives a decolorized product. The reaction is relatively slow but can be accelerated by the addition of small amounts of Pd(II), which acts as a catalyst. The rate of change of the colour intensity IK depends on the amount of catalyst. Pd(II) at concentrations of $0.4\text{-}3 \mu\text{g}/\text{cm}^3$ can be determined if the reaction rate is followed photometrically.

2. Experimental

The dependence of absorbance (A) on time (t) was measured with a Lange photoelectric colorimeter, model J, equipped with a thermostat system [7]. A cell of path - length 25 mm and a filter, $\lambda_{\text{max}}=610 \text{ nm}$, were used. The pH was measured with a Radiometer PHM 29b pH - meter and combined glass-calomel electrode, GK2311C. All solutions were kept in a thermostatic water-bath.

Hydrogen peroxide (2M) was prepared from the 30% reagent. Acetic acid and sodium hydroxide were used for the preparation of acetate buffers [8]. IK solution ($2.8 \cdot 10^{-4}$ M) was made by direct weighting of the solid. Pd(II) solution ($100 \mu\text{g}/\text{cm}^3$) was prepared from a more concentrated PdCl_2 solution and standardized gravimetrically [9]. Analytical-grade reagents, redistilled water and polyethylene vessels were used throughout.

The initial concentration of reactants were put into a 50 cm^3 standard flask, in the order IK, buffer (5 cm^3), catalyst, and water to make up a predetermined volume.

The flask was kept in the thermostat for 5 min, then the solution was made up to the mark with hydrogen peroxide and water and rigorously shaken, and stopwatch was started. The working cell of the colorimeter was first rinsed and the filled with the solution.

The absorbance (A) was measured every 30 sec over a period of 10 min after the hydrogen peroxide was added. Instead of the reaction rate (dc/dt), $d \log A/dt$, which is proportional to it, was determined. $d \log A/dt = \tan \alpha$, where c the concentration of the IK, and $\tan \alpha$ the slope of the linear part of the linear part of the plot A against t .

The initial concentrations of the reagent solutions after dilution to 50 cm^3 were: $2.2 \cdot 10^{-5}$ - $4.2 \cdot 10^{-5}$ M IK, $1.6 \cdot 10^{-2}$ - $16 \cdot 10^{-2}$ M H_2O_2 , 0.4 - $3 \mu\text{g}/\text{cm}^3$ Pd(II).

3. Results and discussion

There is a linear relationship between the $\log A$ of the IK and the initial period of the reaction. Hence the integral variant of the tangent method was used to process the kinetic data [1].

The effect of pH on the catalysed and uncatalysed reaction rates is shown in Fig. 1. It can be seen that the greatest difference in reaction rate is at $\text{pH}=5.0$, where Pd(II) maximally increases the catalytic rate. From Fig. 1, it appears that there is a complicated relationship between the pH and the reaction rate, i.e. the order of reaction is variable with respect to hydrogen-ion concentration for range of concentrations studied. $\text{pH}=5.0$ was chosen as optimal.

The dependence of the reaction rates on the concentration of hydrogen peroxide is shown in Fig. 2, which shows that the uncatalysed reactions is of zero order with respect to the peroxide concentration, whereas the catalytic reaction is of first order with respect to peroxide concentration up to $8.8 \cdot 10^{-2}$ M and of zero order for higher concentrations. For further work a peroxide concentration of $8.8 \cdot 10^{-2}$ M was selected.

The dependence of $\tan \alpha$ on IK concentration is shown in Fig. 3, which shows that with increasing IK concentration the difference in the rates of the catalytic and uncatalysed reactions decreases. Both reactions are of first order with respect to the IK concentration. For further work an IK concentration of $2.8 \cdot 10^{-5}$ M was selected. The rate of catalytic reaction decreases proportionately with increasing IK concentration, probably on account of rivalry the IK and H_2O_2 (HO_2^-) for coordinate linkage in the catalytic activity intermediate complex [10].

Under optimal conditions, concentration of Pd(II) between 0.4 and 3 $\mu\text{g}/\text{cm}^3$ give linear calibration line, as shown in Fig. 4.

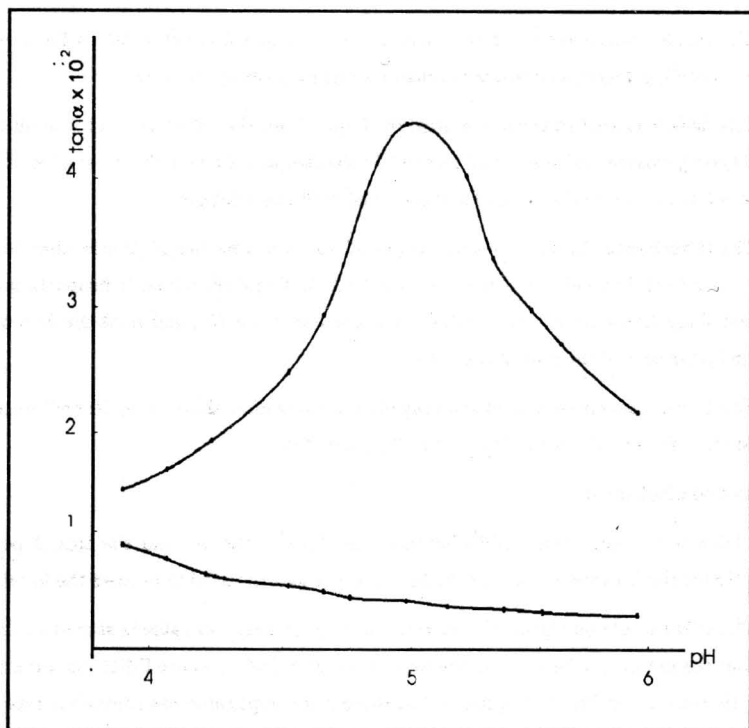


Fig. 1. Dependence of the reaction rate on pH. Initial conditions:
 $IK - 2.8 \times 10^{-5} M$, $H_2O_2 - 8 \times 10^{-2} M$, $Pd(II) - 2 \mu\text{g}/\text{cm}^3$;
 1 - uncatalysed reaction, 2 - catalytic reaction

The dependence between rates and the concentrations of the reactants can be explained by the following kinetic equations (at constant pH).

For the catalytic reaction,

$$- (dc/dt) = Kc_{H_2O_2} c_{IK} c_{Pd(II)} \text{ for } c_{H_2O_2} \leq 8.8 \times 10^{-2} M \text{ and}$$

$$- (dc/dt) = Kc_{IK} c_{Pd(II)} \text{ for } c_{H_2O_2} \geq 8.8 \times 10^{-2} M,$$

where K is a constant proportional to the rate constant of the catalytic reaction.

For the uncatalysed reaction,

$$- (dc/dt) = K_0 c_{IK}$$

where K_0 is a constant proportional to the rate constant of the uncatalysed reaction.

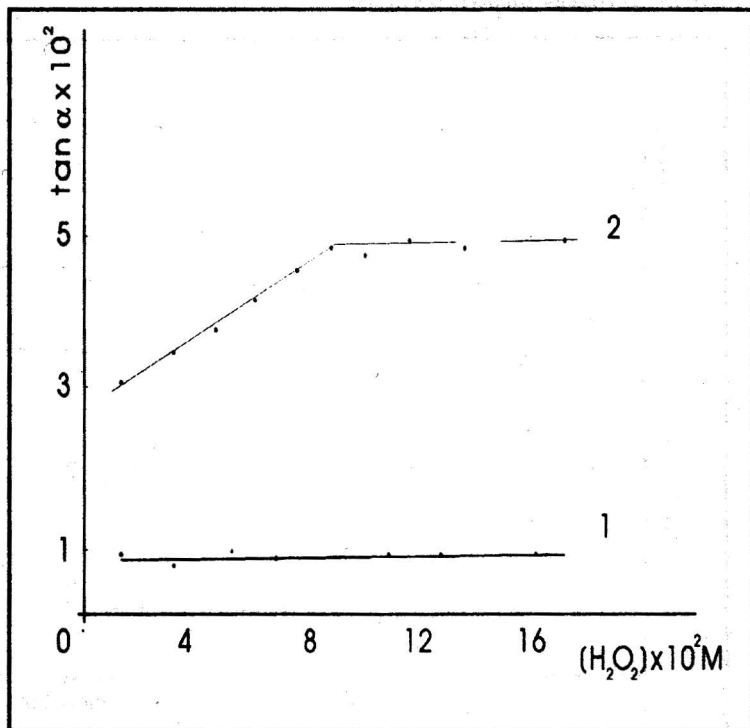


Fig. 2. Dependence of the reaction rate on the H_2O_2 concentration. Initial conditions: $IK - 2.8 \times 10^{-5} M$, $pH - 5.0$, $Pd(II) - 2 \mu g/cm^3$; 1 - uncatalysed reaction, 2 - catalytic reaction

Table I

Pd(II) taken ($\mu g/cm^3$)	Pd(II) found (\bar{x}) ($\mu g/cm^3$)	n	$s \times 10$ ($\mu g/cm^3$)	100 $ts/\bar{x}\sqrt{n}$ %	$(\bar{x} - \mu) \cdot 100 / \mu$ %
3.00	3.06	5	0.93	3.5	2.0
1.60	1.56	5	1.04	7.7	-2.5
0.60	0.54	5	0.72	15.3	-10.0

\bar{x} - mean value; μ - true value; n - number of determinations;

s - standard deviation; *t* - student's *t* for 95% confidence

The accuracy and precision are presented in Table I. The relative error ranges from 3.5 to 15.3% for Pd(II) concentrations from 3 to 0.6 $\mu\text{g}/\text{cm}^3$.

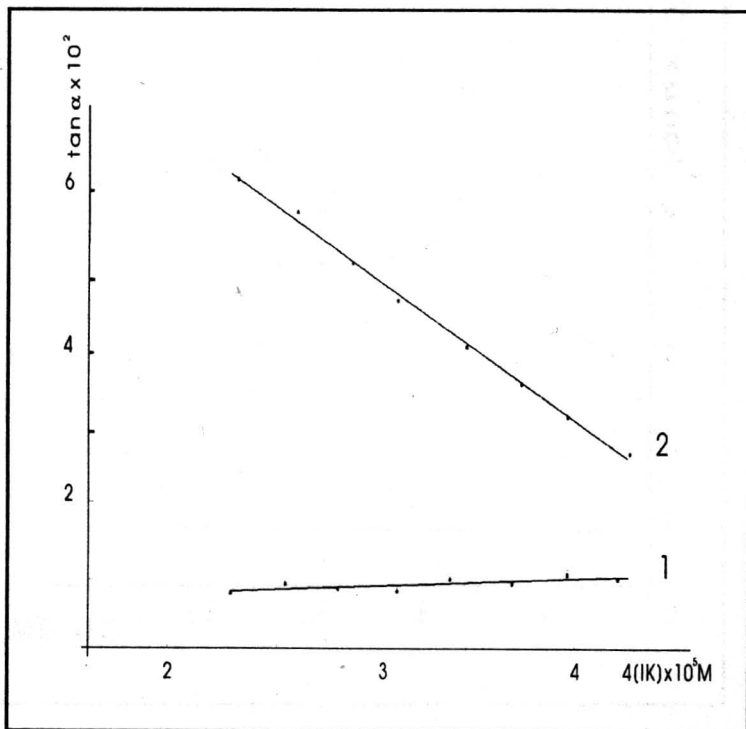


Fig. 3. Dependence of the reaction rate on the IK concentration. Initial conditions: H_2O_2 - $8.8 \times 10^{-2} M$, pH - 5.0, Pd(II) - $2 \mu\text{g}/\text{cm}^3$; 1 - uncatalysed reaction, 2 - catalytic reaction.

To assess the selectivity of the method, the influence of several foreign ions on the catalysed reaction rate was investigated, at a constant Pd(II) concentration of $2 \mu\text{g}/\text{cm}^3$ (Table II). It is seen that Sn^{2+} , tartarate and EDTA (in ratio 1:1 to Pd(II)) interfere. The other ions investigated have practically no influence on the determination of Pd(II) by this method.

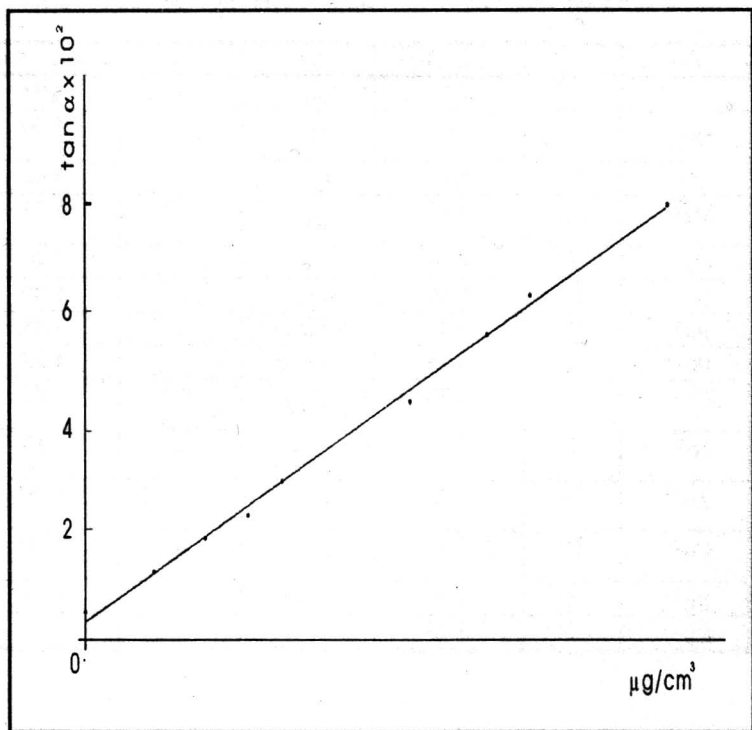


Fig. 4. Dependence of the reaction rate on Pd(II) concentration. Initial conditions: $IK - 2.8 \times 10^{-5} M$, $H_2O_2 - 8.8 \times 10^{-2} M$, $pH - 5.0$.

Table II. Influence of Some Foreign Ions on the Determination of Trace Amounts of Pd(II); $c_{Pd(II)} = 2 \mu\text{g}/\text{cm}^3$; $q = c_{ion}:c_{Pd(II)}$

Ion	q	$\tan\alpha \times 10^2$	Ion	q	$\tan\alpha \times 10^2$
-	-	4.76	Mn ²⁺	10	4.93
NH ₄ ⁺	10	4.66	Hg ²⁺	1	5.40
K ⁺	10	5.13	Fe ³⁺	1	5.46
Mg ²⁺	10 ²	5.13	SO ₄ ⁻	10 ²	5.33
Ca ²⁺	10	4.86	F ⁻	5	4.20
Sr ²⁺	10	4.86	SCN ⁻	10 ⁻¹	5.30
Ba ²⁺	10	5.30	tartarate	1	1.35
Pb ²⁺	10	4.93	citrate	1	4.33
Co ²⁺	1	4.70	HAsO ₄ ²⁻	10 ²	4.80
Ni ²⁺	1	4.93	PO ₄ ³⁻	1	5.13
Zn ²⁺	10	4.73	WO ₄ ²⁻	10 ²	5.06
Cd ²⁺	10	5.06	MoO ₄ ²⁻	10	5.10
Sn ²⁺	1	1.50	EDTA	1	0.75
Cu ²⁺	1	5.13			

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KINETIČKO ODREĐIVANJE MIKROKOLIČINA Pd(II)

T.G. Pecev, R.P. Igov, G.Ž. Miletić, M.N. Miljković

Predložena je nova katalitička reakcija i razrađena nova kinetička metoda za određivanje mikro količina Pd(II) na bazi njihove katalitičke aktivnosti pri oksidaciji indigo karmina vodonik-peroksidom u acetatnom puferu. Osetljivost metode iznosi $0.4 \mu\text{g}/\text{cm}^3$. Greška je ispod 16%, a metoda ima relativno dobru selektivnost.