

K. PACŁAWSKI\*, J. PIWOWOŃSKA\*\*

## KINETICS AND MECHANISM OF THE REDOX REACTION BETWEEN PT(IV) COMPLEX IONS AND SODIUM THIOSULFATE IN AQUEOUS SOLUTION. PART II: NEUTRAL AND ALKALINE SOLUTION

### KINETYKA I MECHANIZM REAKCJI REDOKS POMIĘDZY JONAMI KOMPLEKSOWYMI PT(IV) I TIOSIARCZANEM SODU W ROZTWORZE WODNYM. CZĘŚĆ II: ROZTWÓR OBOJĘTNY I ZASADOWY

In this work, spectrophotometric studies on the kinetics and mechanism of the reaction between  $[\text{PtCl}_6]^{2-}$  complex ions and sodium thiosulfate, in neutral ( $\text{pH} = 7$ ) and alkaline ( $\text{p} = 12$ ) solution, were carried out. Applying different conditions, the influence of initial concentrations of reductant and platinum(IV) complex ions as well as the influence of temperature and ionic strength on the rate constant, was experimentally determined. From the obtained results, the molecularity, the order and the value of enthalpy and entropy of activation of the reaction, were experimentally determined. It was found that in both cases the reduction reaction is relatively slow and in the studied conditions the second-order rate constant changes from  $2.92 \cdot 10^{-2}$  to  $0.40 \text{ M}^{-1}\text{s}^{-1}$  at  $\text{pH} = 7$ , and from  $3.84 \cdot 10^{-2}$  to  $1.55 \text{ M}^{-1}\text{s}^{-1}$  at  $\text{pH} = 12$ . Additionally, depending on the  $\text{pH}$ , different mechanism of the reaction is present. However, regardless on the studied system the only platinum(II) chloride complex ions are the final product of the redox reaction.

*Keywords:* platinum complexes, thiosulfate, redox reaction, kinetics, rate law, rate constant

W pracy, przedstawiono wyniki badań spektrofotometrycznych nad kinetyką i mechanizmem reakcji pomiędzy jonami kompleksowymi  $[\text{PtCl}_6]^{2-}$  i tiosiarczanem sodu, w roztworze obojętnym ( $\text{pH} = 7$ ) i zasadowym ( $\text{pH} = 12$ ). Stosując różne warunki doświadczalne, wyznaczono wpływ stężenia początkowego reduktora oraz stężenia jonów kompleksowych platyny(IV), jak również wpływ temperatury oraz siły jonowej na wartość stałej szybkości reakcji. Na podstawie otrzymanych danych, wyznaczono cząsteczkowość, rząd oraz entalpię i entropię reakcji. Wykazano, że w obydwu przypadkach reakcja redukcji jest stosunkowo wolna. W badanych warunkach wartość drugorzędowej stałej szybkości reakcji ulega zmianie od  $2.92 \cdot 10^{-2}$  do  $0.40 \text{ M}^{-1}\text{s}^{-1}$  w roztworze o  $\text{pH} = 7$ , oraz z  $3.84 \cdot 10^{-2}$  do  $1.55 \text{ M}^{-1}\text{s}^{-1}$  w roztworze o  $\text{pH} = 12$ . Dodatkowo, w zależności od  $\text{pH}$  roztworu, ulega zmianie mechanizm badanej reakcji. Jednakże, bez względu na zastosowane warunki  $\text{pH}$ , produktem końcowym jest zawsze chlorkowy kompleks platyny(II).

## 1. Introduction

In our previous studies on the kinetics and mechanism of reaction between Pt(IV) chloride complex ions in acidic solution [1] we found, that in such conditions, colloidal mixture of Pt and sulfur was obtained. Those studies were the first part of a series of experiments, in which we determined the kinetic and mechanistic factors responsible for precipitation of Pt metallic phase from the aqueous solution. It is still interesting to learn, what kind of conditions favor the reactivity of the Pt(IV) chloride complex ions with the  $\text{Na}_2\text{S}_2\text{O}_3$ , causing the appearance of Pt metallic phase in such a system. One may guess that it is probably associated with the changes in chemical and structural properties of the metal complex ions as well as the reductant under different conditions.

Consequently, in this paper we present our results on the kinetics and mechanism of redox reaction between the  $[\text{PtCl}_6]^{2-}$  ions and  $\text{Na}_2\text{S}_2\text{O}_3$  in neutral and alkaline solutions.

## 2. Experimental

### A. Materials Preparation

Starting solution of  $\text{H}_2\text{PtCl}_6$  was prepared in the way described in our previous work [1]. Obtained "base solution" of Pt(IV) chloride complex ions was next used for experiments.  $\text{Na}_2\text{S}_2\text{O}_3$  solutions were freshly prepared by dilution of the thiosulfate crystals (reagent grade purity, POCh, Gliwice, Poland) in deionized water. All solutions were buffered to adjust the proper  $\text{pH}$ .

### B. Experimental Apparatus

All experiments were performed using Spectrophotometer (UV-2501 PC from Shimadzu, Kyoto, Japan) working in the UV-Vis range (from 190 to 900 nm) using quartz cuvette with the 1 cm optical path, thermostated ( $\pm 0.1^\circ\text{C}$ ) with the Peltier system.

\* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF NON-FERROUS METALS, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

\*\* HYDROMETALLURGY DEPARTMENT, INSTITUTE OF NON-FERROUS METALS IN GLIWICE, 5 SOWINSKIEGO STR., 44-100 GLIWICE, POLAND

### C. Experimental Procedure

Reagents were rapidly mixed in the silica vessel and next placed as fast as possible in the compartment of a spectrophotometer. Next, the changes in spectrum were registered in time. From these results, changes of absorbance values at  $\lambda = 260$  nm (characteristic for  $[\text{PtCl}_6]^{2-}$  ions) in time were collected. Obtained kinetic curves were the base for determination of respective rate constants of the studied reaction. Their values as well as appropriate kinetic equations were determined using TableCurve software [2]. All spectrophotometric experiments were repeated three times. For qualitative determination of the presence of solid particles in the studied systems, except for registration of spectrum in the spectrophotometer, the laser beam was passed through the samples.

### D. Experimental Conditions

The kinetic experiments were carried out under  $\text{pH} = 7$  and  $\text{pH} = 12$ , at constant temperature, reductant concentration as well as concentration of Pt(IV) complex ions. All variants of experimental conditions are gathered in Tab. 1.

TABLE 1  
Conditions, Under Which Experiments Were Carried Out

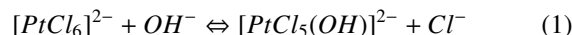
pH	Temperature (°C)	Initial Concentration of Reductant/ $\text{Na}_2\text{S}_2\text{O}_3$ $C_{0,\text{thiosulfate}}$ (M)	Initial Concentration of Pt(IV) Ions $C_{0,\text{Pt(IV)}}$ (M)	Ionic Strength $I$ (M)
Integral Method				
7, 12	25	$5 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	0.1
Dependence of $k_{\text{obs}}$ vs. Reductant Concentration				
7, 12	25	$1 \cdot 10^{-3}$ $2 \cdot 10^{-3}$ $3 \cdot 10^{-3}$ $4 \cdot 10^{-3}$ $5 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	0.1
Initial Rate Method				
7, 12	25	50-fold excess in relation to Pt(IV) concentration	$1 \cdot 10^{-5}$ $1 \cdot 10^{-4}$ $1.9 \cdot 10^{-4}$ $4.9 \cdot 10^{-4}$	0.1
Influence of Ionic Strength				
12	25	$5 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	0.02 NaClO <sub>4</sub> 0.04 NaClO <sub>4</sub> 0.06 NaClO <sub>4</sub> 0.08 NaClO <sub>4</sub> 0.1 NaClO <sub>4</sub>
Influence of Temperature				
12	5 15 25 35 45	$2.5 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	0.1

## 3. Results

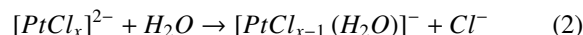
### A. Model of Reaction

It is known from the literature [3] that in acidic solutions containing chloride, platinum(IV) complexes are present in the

form of  $[\text{PtCl}_6]^{2-}$ , which are stable in the solution with  $\text{pH} \leq 8$  [4]. Above this value,  $[\text{PtCl}_6]^{2-}$  ions are transformed into the hydrolyzed form, according to the reaction:



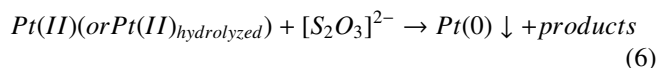
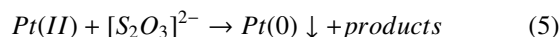
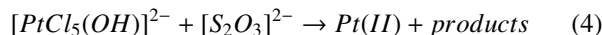
Nachtigall *at all* [5] suggested in his chromatographic studies the existence of different hydrolyzed forms of Pt(IV) in the aqueous solutions. However, nobody provided so far convincing evidence for the presence of these forms. Theoretically, if the pH increases, the complex Pt(IV) ions can be formed according to the reaction:



where the  $x$ , at the beginning, is equal to 6 and is decreasing in the next steps giving the subsequent formulas of adequate hydrolyzed forms of Pt(IV) complexes.

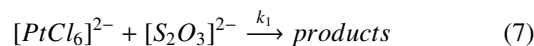
From predominance diagram of dissociated products of  $\text{Na}_2\text{S}_2\text{O}_3$  vs. pH (given in our previous work [1]) it can be seen that in solution with  $\text{pH} = 7 \div 12$ ,  $[\text{S}_2\text{O}_3]^{2-}$  ions dominate. Thus, we can expect that starting form of the reductant is deprotonated bisulfate ion only.

Taking this information into account as well as the literature data [6-14] concerning the species which can be formed during the reaction, we assumed that at  $\text{pH} = 7$  and  $\text{pH} = 12$ , parallel and consecutive paths of the reactions are possible in the scheme of the reaction of Pt(IV) complex ions with thiosulfate. We assumed them as follows:



### B. Spectrophotometric Measurements

After mixing of reactants, spectra of reagents, having the absorption bands with maximum at  $\lambda = 260$  nm (characteristic for  $[\text{PtCl}_6]^{2-}$  ions) and  $\lambda = 217$  nm (characteristic for sodium thiosulfate) disappeared, confirming the presence of the reaction between both reactants, i.e. reaction (3):



### C. Molecularity of Elementary Reaction

In order to determine the molecularity of the first stage of the studied reaction in the solution with  $\text{pH} = 7$ , the integral method was used with the 20-fold excess of reductant with respect to the concentration of Pt(IV) complex ions. In such a case, for the reaction (7) the rate equation describing disappearance of Pt(IV) ions in the system can be written as follows:

$$-\frac{dC_{[\text{PtCl}_6]^{2-}}}{dt} = k_{\text{obs}} C_{[\text{PtCl}_6]^{2-}}^n \quad (8)$$

where:

$$k_{\text{obs}} = k C_{[\text{S}_2\text{O}_3]^{2-}}^m \quad (9)$$

The fitting procedure using TC Curve as well as a graphical interpretation (Fig. 1) of kinetic results (after analytical solution

of eq. (8) with the assumption  $n = 1$ ) confirm the first-order character of this reaction. Taking into account the isolation conditions the pseudo-first order kinetics of reaction can be suggested and the reaction between Pt(IV) and thiosulfate is bimolecular.

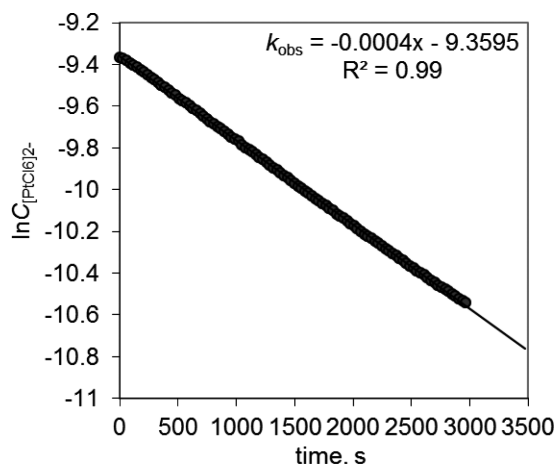
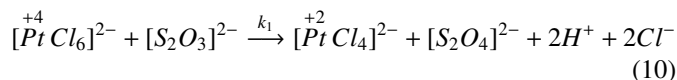


Fig. 1. An example of  $\ln C_{Pt(IV)}$  vs. time dependence for the reaction between the  $[PtCl_6]^{2-}$  ion and sodium thiosulfate. Conditions: pH = 7,  $C_{0,[PtCl_6]^{2-}} = 1 \cdot 10^{-4}$  M,  $C_{0,thiosulfate} = 2 \cdot 10^{-3}$  M, temperature 25°C

Hence, the reduction reaction of Pt(IV) complex ions at pH = 7 can be described with only one equation:



In the solution with pH = 12 the graphical approach failed to yield linear dependence. Thus, further fitting procedure was carried out using TC Curve software which gave the form of the rate equation in the following form:

$$Abs(\propto C_{[PtCl_6]^{2-}}) = a \exp(-bt) + c \exp(-dt) \quad (11)$$

Constant  $b$  and  $d$  in eq. (11) are the respective rate constants ( $k_2$  and  $k_3$ ) of two parallel processes. Each of them is described by one-exponential function. Taking into account the obtained equation it can be suggested, that the reaction of  $[PtCl_6]^{2-}$  ions takes place via two parallel paths. Because in the solution with pH = 12, only one form of reductant is present, except for the reduction of Pt(IV) ions, the another parallel reaction describe probably the Pt(IV) hydrolysis. Thus, it is likely that the mechanism of the reaction path can be described with equations (10) and (1) taking place simultaneously.

#### D. Effect of Reductant Concentration on the Observed Rate Constant

The kinetic measurements were performed with increasing amount of reductant in the solution having two different pH = 7 and 12. Calculated values of the observed rate constants are gathered in Table 2.

According to the equation (9),  $k_{obs}$  should be proportional to the concentration of reductant ( $C_{reductant}$ ) to the power  $m$ . It can be seen from our results that in both series of experiments (for pH = 7 and 12)  $k_{obs}$  vs. reductant concentration dependencies had linear character (Fig. 2a and 2b) which suggest  $m = 1$  for the both studied systems.

TABLE 2  
Values of the Observed Rate Constant of  $[PtCl_6]^{2-}$  Reaction with Sodium Thiosulfate at Different Concentration of Reductant.

Conditions: pH = 7 and 12,  $C_{0,[PtCl_6]^{2-}} = 1 \cdot 10^{-4}$  M, Temperature = (25±0.1)°C, Ionic Strength = 0.1 M NaClO<sub>4</sub>

Concentration of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> C <sub>reductant</sub> (M)	The Rate Constant $k_{obs} \cdot 10^3$ (Average of Four Experiments) (s <sup>-1</sup> )	Mean Standard Deviation $\sigma \cdot 10^3$ (s <sup>-1</sup> )
pH = 7		
1 · 10 <sup>-3</sup>	0.41	0.01
2 · 10 <sup>-3</sup>	0.78	0.01
3 · 10 <sup>-3</sup>	1.15	0.03
4 · 10 <sup>-3</sup>	1.55	0.04
5 · 10 <sup>-3</sup>	1.95	0.06
pH = 12		
1 · 10 <sup>-3</sup>	0.430	0.005
2 · 10 <sup>-3</sup>	0.750	0.003
3 · 10 <sup>-3</sup>	0.999	0.006
4 · 10 <sup>-3</sup>	1.33	0.01
5 · 10 <sup>-3</sup>	1.72	0.03

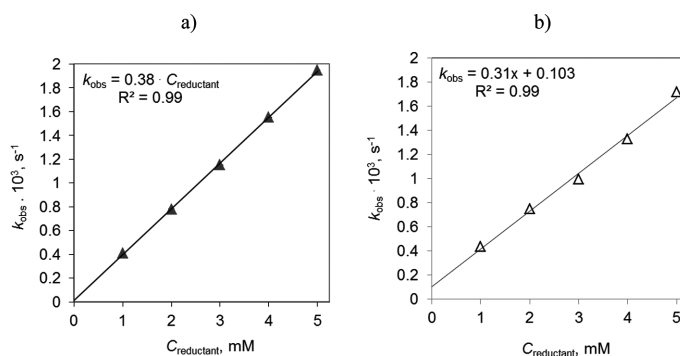


Fig. 2. Dependence of the  $k_{obs}$  vs.  $C_{reductant}$  for the reaction of  $[PtCl_6]^{2-}$  with sodium thiosulfate at different conditions of pH: (a) – pH = 7, (b) – pH = 12. Conditions:  $C_{0,[PtCl_6]^{2-}} = 1 \cdot 10^{-4}$  M, temperature 25°C

When the reaction takes place at pH = 7, the intercept of  $k_{obs}$  vs.  $C_{reductant}$  dependence with the Y axis was localized at the initial point (0,0) of the system. Therefore, it was assumed that under these conditions, the mechanism of  $[PtCl_6]^{2-}$  ions reduction can be described by the single reaction (10).

However, in case of pH = 12 (Fig. 2b), extrapolation of this dependence to the “zero concentration” of the reductant, yields an intercept with the  $k'$  value at Y axis. After substitution of the empirical linear equation shown in Fig. 2b into equation (8), we can obtain the rate equation in the form:

$$-\frac{dC_{Pt(IV)}}{dt} = k_1 C_{[PtCl_6]^{2-}} C_{[S_2O_3]^{2-}} + k' C_{[PtCl_6]^{2-}} \quad (12)$$

where,  $k_2 = 0.3147 \text{ M}^{-1} \cdot \text{s}^{-1}$  and  $k' = 1 \cdot 10^{-4} \text{ s}^{-1}$ . The second term of this equation suggests that simultaneously

with the reduction of Pt(IV) ions, they can also disappear due to parallel reaction:



Taking into account alkaline solution and very slow disappearance of the absorption bands at 260 nm without the presence of the reductant it is likely that parallel process is the hydrolysis of  $[\text{PtCl}_6]^{2-}$  (eq. 1). In fact, due to the large excess of  $\text{OH}^-$  ions ( $C_{\text{OH}^-} = 0.1$ ) as compare to Pt(IV) concentration present in the system,  $k'$  in the equation (8) is equal to:

$$k' = k_3 C_{\text{OH}^-} \quad (14)$$

This equation confirms the presence of two bimolecular reactions taking part in the system. From the obtained results, the value of the second-order rate constant of Pt(IV) hydrolysis ( $k_2$ ) is derived and is equal to  $1 \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ .

### E. Effect of Ionic Strength

Experiments were carried out at pH = 7 and 12, for different  $I$ , which was changed from 0.02 to 0.1 M. The obtained results of the rate constants are gathered in Table 3.

TABLE 3  
Values of the Rate Constant of  $[\text{PtCl}_6]^{2-}$  Reaction with Sodium Thiosulfate at Different Ionic Strength. Conditions: pH = 12,  $C_{[\text{PtCl}_6]^{2-}} = 1 \cdot 10^{-4} \text{ M}$ , temperature =  $(25 \pm 0.1)^\circ\text{C}$

Concentration of Reductant $C_{\text{reductant}}$ (M)	The Rate Constant $k_{\text{obs}} \cdot 10^3$ (Average of Four Experiments) ( $\text{s}^{-1}$ )	Mean Standard Deviation $\sigma \cdot 10^3$ ( $\text{s}^{-1}$ )
pH = 7		
0.02	2.20	0.01
0.04	2.36	0.02
0.06	2.59	0.01
0.08	2.76	0.01
0.10	2.96	0.01
pH = 12		
0.02	2.36	0.02
0.04	2.73	0.03
0.06	3.32	0.02
0.08	3.48	0.01
0.10	3.83	0.05

Taking into account the Brönstedt-Bjerrum (B-B) equation:

$$\log\left(\frac{k_{\text{obs}}}{k_{0,\text{obs}}}\right) = z_A z_B A \left(\frac{\sqrt{I}}{1 + \sqrt{I}}\right) \quad (15)$$

where  $z_A$ ,  $z_B$  are the charges of reagents and  $A = 0.509$  (constant value for the aqueous solution) it can be clearly seen, that for the reaction conducted at increasing ionic strength and at adjusted pH (7 and 12), in both cases reactions were accelerated (Fig. 3a and 3b). The positive slope of B-B dependencies as well as negative charge of the  $[\text{PtCl}_6]^{2-}$  ions clearly indicate

that in both cases charge of reductant species have also negative sign. Comparing the calculated and experimental results (Fig. 3a and 3b) it can be assumed that in the studied system charges of reacting species are close to “- 1”.

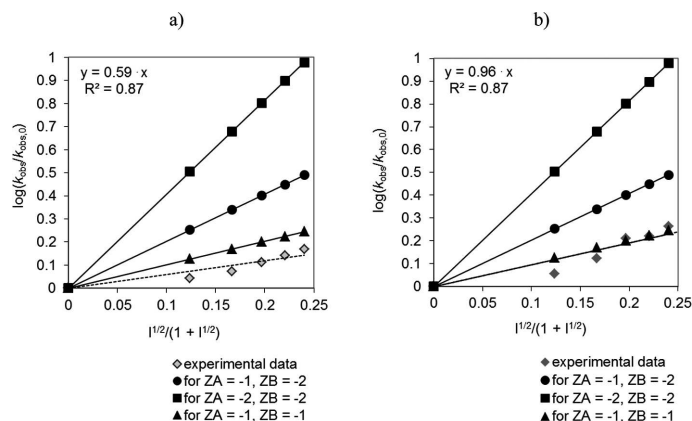
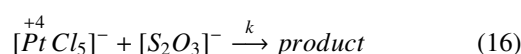


Fig. 3. Salt effect for the redox reaction between  $[\text{PtCl}_6]^{2-}$  ion and sodium thiosulfate according to Brönstedt-Bjerrum dependence ( $\log(k_{\text{obs}}/k_{\text{obs},0})$  vs.  $I^{1/2}/(1+I^{1/2})$ ) at different pH: a) pH = 7; b) pH = 12; temperature  $25^\circ\text{C}$

Consequently, in order to be in agreement with the experimental data, the complex Pt(IV) ions should coordinate five chloride (or hydroxyl) ligands. Thus, in the systems with pH = 7 and 12, the mechanism of the reaction can be also described as:



In order to confirm the presence of reaction (16), it is necessary to detect the structure of suggested reactants.

### F. The Order of Reaction

To determine the order of the studied reaction with respect to  $[\text{PtCl}_6]^{2-}$  ions, an initial rate method was applied. From experiments, values of the rate constant were determined (Table 4) for four different initial concentrations of  $[\text{PtCl}_6]^{2-}$  ions.

TABLE 4  
Values of the Rate Constant of  $[\text{PtCl}_6]^{2-}$  Reaction with Sodium Thiosulfate at Different Initial Concentration of Platinum(IV) Complexes. Conditions:  $C_{0,\text{Na}_2\text{S}_2\text{O}_3} = 5 \cdot 10^{-3} \text{ M}$ , pH = 7, temperature =  $(25 \pm 0.1)^\circ\text{C}$ , Ionic Strength = 0.1 M  $\text{NaClO}_4$

Initial Concentration of $[\text{PtCl}_6]^{2-}$ $C_{\text{reductant}}$ (M)	The Rate Constant $k_{\text{obs}} \cdot 10^3$ (Average of Four Experiments) ( $\text{s}^{-1}$ )	Mean Standard Deviation $\sigma \cdot 10^3$ ( $\text{s}^{-1}$ )	The Second Order Rate Constant $k_1$ (Average of Four Experiments) ( $\text{M}^{-1} \cdot \text{s}^{-1}$ )	Mean Standard Deviation $\sigma$ ( $\text{M}^{-1} \cdot \text{s}^{-1}$ )
$5 \cdot 10^{-5}$	1.76	0.47	0.352	0.009
$1 \cdot 10^{-4}$	1.95	0.01	0.390	0.001
$1.9 \cdot 10^{-4}$	1.98	0.10	0.396	0.004
$4.9 \cdot 10^{-4}$	2.01	0.02	0.402	0.005

Assuming that the differential rate equation of  $[\text{PtCl}_6]^{2-}$  ions reduction has the form of eq. (8), it can be suggested

that in the initial period of time, the rate ( $v_0$ ) is described by equation:

$$v_0 = k_{obs} C_{[PtCl_6]^{2-}}^n \quad (17)$$

Taking the logarithm of equation (17), a linear dependence can be obtained:

$$\log v_0 = \log k_{obs} + n \log C_{0,[PtCl_6]^{2-}} \quad (18)$$

The slope ( $n$ ) of the obtained dependence defines the order of the studied reaction with respect to  $[PtCl_6]^{2-}$  species. Experimentally obtained results, for two different pH (7 and 12) of the solution, were described with equation (18), and are shown in Fig. 4a and 4b. It can be seen that in case of Pt(IV) reduction at pH = 7, a straight line is obtained (Fig. 4a) with the slope close to unity ( $n = 0.94$ ). It means that the order of reaction with respect to  $[PtCl_6]^{2-}$  ions equals to one, and it is likely that the rate equation of the first elementary step has the following form:

$$-\frac{dC_{[PtCl_6]^{2-}}}{dt} = k C_{[PtCl_6]^{2-}}^1 C_{reductant} \quad (19)$$

For reduction of Pt(IV) ions in aqueous solution at pH = 12,  $\log v_0$  vs.  $C_{0,[PtCl_6]^{2-}}$  dependence was found to be non-linear. It confirms that in this environment mechanism of the reaction is complex and the determination of the order by the initial rate method is not possible.

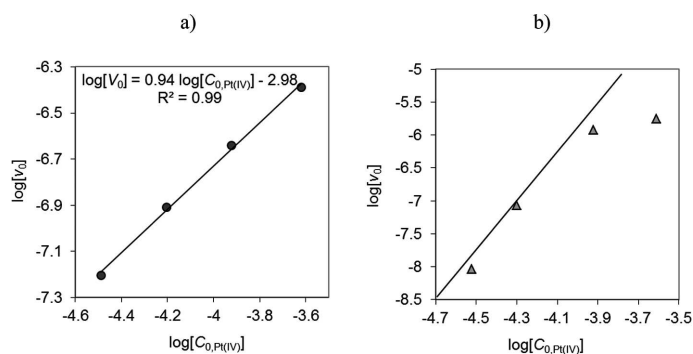


Fig. 4. Dependence of  $\log(v_0)$  vs.  $\log(C_{0,Pt(IV)})$  for the reaction of  $[PtCl_6]^{2-}$  with sodium thiosulfate at different conditions: a) pH = 7, b) pH = 12 (temperature 25°C)

#### G. Effect of Temperature

Influence of temperature on the kinetics of redox reaction between  $[PtCl_6]^{2-}$  and sodium thiosulfate was studied in the solution with pH = 12, in the range from 5 to 45°C. Obtained values of the rate constants are gathered in Table 5.

TABLE 5

The second order rate constant of the reduction reaction of  $[PtCl_6]^{2-}$  with sodium thiosulfate obtained at different temperatures

Temperature (K)	Rate Constant (Average of Four Experiments), $k$ ( $M^{-1} \cdot s^{-1}$ )	Mean Standard Deviation $\sigma$ ( $M^{-1} \cdot s^{-1}$ )
pH = 12		
278	0.1168	0.01013
288	0.2319	0.00284
298	0.4344	0.09504
308	0.6940	0.04608
318	1.5530	0.04759

Determined rate constants were used to calculate  $\Delta H^*$  (enthalpy of activation) and  $\Delta S^*$  (entropy of activation) for the studied reaction. Applying logarithmic form of Eyring equation [15] (Fig. 5), from the, the values of these parameters were calculated, and they are gathered in Table 6.

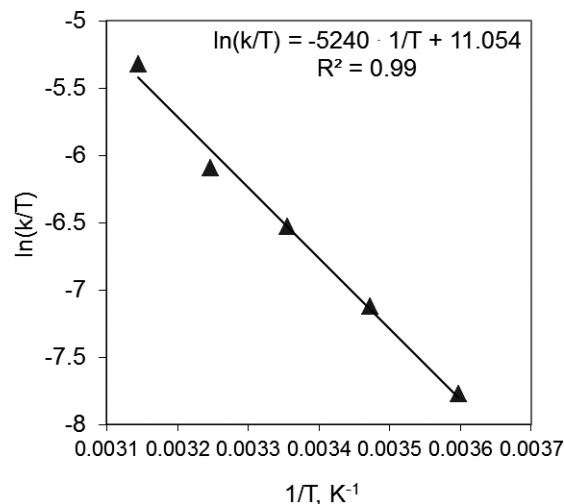


Fig. 5. An example of the Eyring plot for the reaction of  $[PtCl_6]^{2-}$  reduction at pH = 12

TABLE 6

The Parameters in Eyring Equation for the Reaction Between  $[PtCl_6]^{2-}$  Ions and Sodium Thiosulfate

pH	$23.759 + \Delta S^*$	$\Delta H^*/R$	Enthalpy of Activation $\Delta H^*$ ( $kJ \cdot mol^{-1}$ )	Entropy of Activation $\Delta S^*$ ( $J \cdot mol^{-1} \cdot K^{-1}$ )
12	11.054	5240	43.56	- 105.6

#### 4. Discussion

Knowing the complexing properties of thiosulfate in relation to Au(I) chloride ions as well as their potential reducing properties with respect to Pt(IV) chloride complex ions, we used  $Na_2S_2O_3$  with a hope to find conditions for selective reduction of Pt(IV) ions to metallic form in the presence of gold ions.

It is evident from spectroscopic studies that in neutral and alkaline solution the first step of the reaction leads to the disappearance of  $[PtCl_6]^{2-}$  ions in the system. It was also observed that in the alkaline solutions (pH = 12), after long period of time (ca. 24 hours) spectra of  $[PtCl_6]^{2-}$  ions disappear without the presence of sodium thiosulfate. Thus, it was assumed that hydrolysis of Pt(IV) complex ions can take place under such conditions. Probably, these hydrolyzed species of Pt(IV) can be also reduced with  $Na_2S_2O_3$ . Spectral analysis of the reacting system suggest the form of the product of platinum(IV) chloride complex reduction. It can be very likely that the absorbance band with maximum at  $\lambda = 238$  nm present after the reaction belongs to platinum(II) chloride complex ions ( $[PtCl_4]^{2-}$ ) which appears in the system. It is also likely that these complex ions can hydrolyze at pH = 12 following substitution mechanism (chloride ligands are exchanged with the hydroxyl ions).

Experimentally obtained kinetic data, enable us to discuss further on the possible mechanism of the studied reaction. It was found that in the neutral and alkaline solution the first elementary step of platinum(IV) complex ions reduction (Fig. 1 and Fig. 2a) has bimolecular character. Taking into account a distribution of reductant species as a function of pH (see [1]) as well as possible hydrolysis of  $[\text{PtCl}_6]^{2-}$  in the solution with pH = 12, the parallel path of the reaction appears in the studied system. The presence of the parallel paths of reaction can be also suggested from the  $k_{obs}$  vs.  $C_{reductant}$  dependence (Fig. 2b). The interception of the Y axis, which changes the formula of observed rate constant into:

$$k_{obs} = kC_{reductant} + k' \quad (20)$$

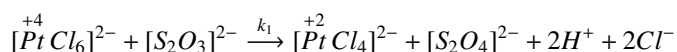
suggests a disappearance of the Pt(IV) ions with the rate constant  $k'$  without participation of any form of reductant. In such a case, two forms of the precursor can react with the  $[\text{S}_2\text{O}_3]^{2-}$  ions (eq. 4 and 10). Summarizing this part of our discussion, it can be stated that by applying different acidity in the system, the mechanism of Pt(IV) complex ions reduction changes. In the solution with pH = 7, only one reaction takes place in the system: platinum(IV) chloride ions may react with the unprotonated form of reductant. In alkaline solution (pH = 12), two parallel steps of this reaction exist.

Suggestions about differences between both studied systems can be also taken from the differences in the values of enthalpy and entropy of activation. The comparison of these values for pH = 7 and pH = 12 shows the increase of  $\Delta H^*$  from 35.91 to 43.56  $\text{kJ} \cdot \text{mol}^{-1}$ , and the increase of  $\Delta S^*$  from -129.5 to -105.6  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , respectively. The change of  $\Delta S^*$  value suggests the appearance of more disordered intermediate product during Pt(IV) ions reduction in the studied systems.

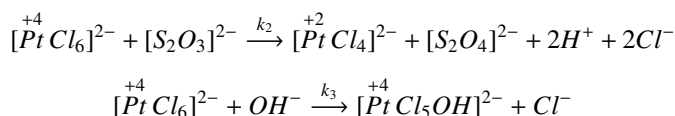
Analyzing obtained experimental data as well as considering above discussion we can conclude that sodium thiosulfate can be a potential reductant of  $[\text{PtCl}_6]^{2-}$  ions. However, in the neutral and alkaline solutions the final product of this reduction is always platinum complex with Pt on the second valence state.

## 5. Conclusions

- No precipitation of the solid phase at pH = 7 and 12 was detected in the system  $[\text{PtCl}_6]^{2-} + \text{Na}_2\text{S}_2\text{O}_3$ . This fact suggests the lack of the Pt(II) complex reduction step (eq. 4 and eq. 5) in the model of reaction.
- The mechanism of the studied reaction strongly depends on pH of the solution. Different forms of a precursor ( $[\text{PtCl}_6]^{2-}$  and hydrolyzed species, e.g.  $[\text{PtCl}_5\text{OH}]^-$ ) can take part in the redox reaction with only one form of reductant ( $[\text{S}_2\text{O}_3]^{2-}$ ).
- The suggested mechanism of the reaction in neutral solutions (pH = 7), can be described by the bimolecular reaction:



- In alkaline solutions (pH = 12), the mechanism of Pt(IV) reaction can be described by the two parallel bimolecular reactions, i.e. reduction reaction and hydrolysis of Pt(IV) complexes:



- The integral form of the rate equation for the studied reaction can be given in the form:
  - in neutral solution:
 
$$C_{[\text{PtCl}_6]^{2-}} = C_{0,[\text{PtCl}_6]^{2-}} \exp(-k_{obs}t)$$
 (values of  $k_{obs}$  at 25°C are given in the Table 2-4)
  - in alkaline solution:
 
$$C_{[\text{PtCl}_6]^{2-}} = C_{0,[\text{PtCl}_6]^{2-}} \exp\left(-Te^{(11.054-5240\frac{1}{T})}t\right)$$
 The term in the rate equation associated with the hydrolysis reaction can be neglected due to the order of magnitude lower value of the hydrolysis rate constant ( $k_3$ ) as compared with the rate constant ( $k_2$ ) for the step of reduction.
- The order of reaction with respect to Pt(IV) ions in neutral solution is equal to "1".

## Acknowledgements

This work was supported by the Ministry of Education and Science (Department of Scientific Researches), Poland, under Grant No. 3 T08B 015 29.

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