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 (pH = 7) and alkaline (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 pH = 7, and from 3.84 \cdot 10^{-2} to 1.55 \text{ M}^{-1} \text{s}^{-1} at pH = 12. Additionally, depending on the 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

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 Na\(_2\)S\(_2\)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 Na\(_2\)S\(_2\)O\(_3\) in neutral and alkaline solutions.

2. Experimental

A. Materials Preparation

Starting solution of H\(_3\)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. Na\(_2\)S\(_2\)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 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 (±0.1°C) with the Peltier system.
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 pH = 7 and 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>
<thead>
<tr>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Initial Concentration of Reductant/Na2S2O3</th>
<th>Initial Concentration of Pt(IV) Ions</th>
<th>Ionic Strength I ′ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C0_thiosulfate (M)</td>
<td>C0_Pt(IV) (M)</td>
<td></td>
</tr>
<tr>
<td>7, 12</td>
<td>25</td>
<td>5.10^{-3}</td>
<td>1.10^{-4}</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Dependence of kobs vs. Reductant Concentration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7, 12</td>
<td>25</td>
<td>1.10^{-3}</td>
<td>1.10^{-4}</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Initial Rate Method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7, 12</td>
<td>25</td>
<td>50-fold excess in relation to Pt(IV) concentration</td>
<td>1.10^{-3}</td>
<td>1.9.10^{-4}</td>
</tr>
<tr>
<td></td>
<td>Influence of Ionic Strength</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>25</td>
<td>5.10^{-3}</td>
<td>1.10^{-4}</td>
<td>0.02 NaClO4</td>
</tr>
<tr>
<td></td>
<td>Influence of Temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>2.5.10^{-3}</td>
<td>1.10^{-4}</td>
<td>0.04 NaClO4</td>
</tr>
</tbody>
</table>

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 pH \( \leq 8 \) [4]. Above this value, \([\text{PtCl}_6]^{2-}\) ions are transformed into the hydrolyzed form, according to the reaction:

\[
[\text{PtCl}_6]^{2-} + \text{OH}^- \leftrightarrow [\text{PtCl}_5(\text{OH})]^{2-} + \text{Cl}^- \quad (1)
\]

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:

\[
[\text{PtCl}_x]^{2-} + \text{H}_2\text{O} \rightarrow [\text{PtCl}_{x-1}(\text{H}_2\text{O})]^{2-} + \text{Cl}^- \quad (2)
\]

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 pH \( \approx 7 \div 12 \), \([\text{S}_2\text{O}_3]^{2-}\) 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 pH = 7 and 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:

\[
[\text{PtCl}_6]^{2-} + [\text{S}_2\text{O}_3]^{2-} \rightarrow \text{Pt(II)} + \text{products} \quad (3)
\]

\[
[\text{PtCl}_5(\text{OH})]^{2-} + [\text{S}_2\text{O}_3]^{2-} \rightarrow \text{Pt(II)} + \text{products} \quad (4)
\]

\[
\text{Pt(II)} + [\text{S}_2\text{O}_3]^{2-} \rightarrow \text{Pt(0)} \downarrow + \text{products} \quad (5)
\]

\[
\text{Pt(II)(orPt(II)hydrolyzed)} + [\text{S}_2\text{O}_3]^{2-} \rightarrow \text{Pt(0)} \downarrow + \text{products} \quad (6)
\]

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):

\[
[\text{PtCl}_6]^{2-} + [\text{S}_2\text{O}_3]^{2-} \rightarrow \text{products} \quad (7)
\]

C. Molecularity of Elementary Reaction

In order to determine the molecularity of the first stage of the studied reaction in the solution with 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:

\[
\frac{d[\text{PtCl}_6]^{-}}{dt} = -k_{\text{obs}}\text{C}_{[\text{PtCl}_6]}^{-} \quad (8)
\]

where:

\[
k_{\text{obs}} = k_{\text{m}}\text{C}_{[\text{S}_2\text{O}_3]}^{-}. \quad (9)
\]

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 $a = 1$ 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.

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

$$^{+4}[PtCl_6]^{2-} + [S_2O_3]^{2-} \rightarrow ^{+2}[PtCl_4]^{2-} + [S_2O_4]^{2-} + 2H^+ + 2Cl^-$$

(10)

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:

$$A(hs) \propto C_{[PtCl_4]^{2-}} = a \exp(-bt) + c \exp(-dt)$$

(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 ($C_{reduc,tan}$) 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>
<thead>
<tr>
<th>Concentration of Na$_2$S$_2$O$_3$</th>
<th>The Rate Constant $k_{obs}$</th>
<th>Mean Standard Deviation $\sigma t \cdot 10^2$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{reduc,tan}$ (M)</td>
<td>(Average of Four Experiments)</td>
<td></td>
</tr>
<tr>
<td>pH = 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 $\cdot 10^{-3}$</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td>2 $\cdot 10^{-3}$</td>
<td>0.78</td>
<td>0.01</td>
</tr>
<tr>
<td>3 $\cdot 10^{-3}$</td>
<td>1.15</td>
<td>0.03</td>
</tr>
<tr>
<td>4 $\cdot 10^{-3}$</td>
<td>1.55</td>
<td>0.04</td>
</tr>
<tr>
<td>5 $\cdot 10^{-3}$</td>
<td>1.95</td>
<td>0.06</td>
</tr>
<tr>
<td>pH = 12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 $\cdot 10^{-3}$</td>
<td>0.430</td>
<td>0.005</td>
</tr>
<tr>
<td>2 $\cdot 10^{-3}$</td>
<td>0.750</td>
<td>0.003</td>
</tr>
<tr>
<td>3 $\cdot 10^{-3}$</td>
<td>0.999</td>
<td>0.006</td>
</tr>
<tr>
<td>4 $\cdot 10^{-3}$</td>
<td>1.33</td>
<td>0.01</td>
</tr>
<tr>
<td>5 $\cdot 10^{-3}$</td>
<td>1.72</td>
<td>0.03</td>
</tr>
</tbody>
</table>

When the reaction takes place at pH = 7, the intercept of $k_{obs}$ vs. $C_{reduc,tan}$ dependence with the Y axis was localized at $0.038$ and the slope is $0.99$, thus $m = 1$. This means, that under these conditions, the mechanism of $[PtCl_6]^{2-}$ reduction can be described by the single reaction (10).

However, in case of pH = 12 (Fig. 2b), extrapolation of the rate constant $k_{obs}$ with sodium thiosulfate at different concentrations of pH (a) - pH = 7, (b) - pH = 12. Conditions: $C_{[PtCl_4]^{2-}} = 1 \cdot 10^{-4}$ M, temperature 25°C

$$-\frac{dC_{Pt(IV)}}{dt} = k_1C_{[PtCl_4]^{2-}}C_{[S_2O_3]^{2-}} + k' C_{[PtCl_6]^{2-}}$$

(12)

where, $k_2 = 3.147$ M$^{-1}$ s$^{-1}$ and $k' = 1 \cdot 10^{-4}$ 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:

\[ [\text{PtCl}_6]^{2-} \rightarrow \text{products} \]  \quad \text{(13)}

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 [PtCl₆]^{2-} (eq. 1). In fact, due to the large excess of OH⁻ ions (COH⁻ = 0.1) as compared to Pt(IV) concentration present in the system, k’ in the equation (8) is equal to:

\[ k' = k_3C_{OH^-} \]  \quad \text{(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 (k₂) is derived and is equal to 1 · 10⁻⁵ M⁻¹ 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 [PtCl₆]^{2-} Reaction with Sodium Thiosulfate at Different Ionic Strength.

<table>
<thead>
<tr>
<th>Concentration of Reductant</th>
<th>The Rate Constant k_{obs} 10^{10} (Average of Four Experiments) (s⁻¹)</th>
<th>Mean Standard Deviation σ · 10^3 (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>2.20</td>
<td>0.01</td>
</tr>
<tr>
<td>0.04</td>
<td>2.36</td>
<td>0.02</td>
</tr>
<tr>
<td>0.06</td>
<td>2.59</td>
<td>0.01</td>
</tr>
<tr>
<td>0.08</td>
<td>2.76</td>
<td>0.01</td>
</tr>
<tr>
<td>0.10</td>
<td>2.96</td>
<td>0.01</td>
</tr>
<tr>
<td>pH = 12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>2.36</td>
<td>0.02</td>
</tr>
<tr>
<td>0.04</td>
<td>2.73</td>
<td>0.03</td>
</tr>
<tr>
<td>0.06</td>
<td>3.32</td>
<td>0.02</td>
</tr>
<tr>
<td>0.08</td>
<td>3.48</td>
<td>0.01</td>
</tr>
<tr>
<td>0.10</td>
<td>3.83</td>
<td>0.05</td>
</tr>
</tbody>
</table>

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

\[ \log \left( \frac{k_{obs}}{k_{0,obs}} \right) = 2z_Az_BA \left( \frac{\sqrt{I}}{1 + \sqrt{I}} \right) \]  \quad \text{(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 [PtCl₆]^{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”.

F. The Order of Reaction

To determine the order of the studied reaction with respect to [PtCl₆]^{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 [PtCl₆]^{2-} ions.

Table 4: Values of the Rate Constant of [PtCl₆]^{2-} Reaction with Sodium Thiosulfate at Different Initial Concentration of Platinum(IV) Complexes.

<table>
<thead>
<tr>
<th>Initial Concentration of [PtCl₆]^{2-} (M)</th>
<th>The Rate Constant k_{obs} 10^{10} (Average of Four Experiments) (s⁻¹)</th>
<th>Mean Standard Deviation σ · 10^3 (s⁻¹)</th>
<th>The Second Order Rate Constant k₁ 10^{10} (Average of Four Experiments) (M⁻¹ s⁻¹)</th>
<th>Mean Standard Deviation σ 10^3 (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 · 10⁻⁵</td>
<td>1.76</td>
<td>0.47</td>
<td>0.352</td>
<td>0.009</td>
</tr>
<tr>
<td>1 · 10⁻⁴</td>
<td>1.95</td>
<td>0.01</td>
<td>0.390</td>
<td>0.001</td>
</tr>
<tr>
<td>1.9 · 10⁻⁴</td>
<td>1.98</td>
<td>0.10</td>
<td>0.396</td>
<td>0.004</td>
</tr>
<tr>
<td>4.9 · 10⁻⁴</td>
<td>2.01</td>
<td>0.02</td>
<td>0.402</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Assuming that the differential rate equation of [PtCl₆]^{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:

\[
v_0 = k_{obs} C_{[PtCl_6]^{2-}}^{n}
\]  

(17)

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

\[
\log v_0 = \log k_{obs} + n \log C_{[PtCl_6]^{2-}}
\]  

(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:

\[
-\frac{dC_{[PtCl_6]^{2-}}}{dt} = k C_{[PtCl_6]^{2-}}^{1} C_{\text{reductant}}
\]  

(19)

For reduction of Pt(IV) ions in aqueous solution at pH = 12, \( \log v_0 \) vs. \( C_{[PtCl_6]^{2-}} \) 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.

![Dependence of log(v0) vs. log(C0)](image)

Fig. 4. Dependence of \( \log(v_0) \) vs. \( \log(C_{[PtCl_6]^{2-}}) \) 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

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Rate Constant ( k ) (Average of Four Experiments), ( \text{M}^{-1} \cdot \text{s}^{-1} )</th>
<th>Mean Standard Deviation ( \sigma ) ( \text{M}^{-1} \cdot \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>278</td>
<td>0.1168</td>
<td>0.01013</td>
</tr>
<tr>
<td>288</td>
<td>0.2319</td>
<td>0.00284</td>
</tr>
<tr>
<td>298</td>
<td>0.4344</td>
<td>0.09504</td>
</tr>
<tr>
<td>308</td>
<td>0.6940</td>
<td>0.04608</td>
</tr>
<tr>
<td>318</td>
<td>1.5530</td>
<td>0.04759</td>
</tr>
</tbody>
</table>

Determined rate constants were used to calculate \( \Delta H^\circ \) (enthalpy of activation) and \( \Delta S^\circ \) (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.

**TABLE 6**

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

<table>
<thead>
<tr>
<th>pH</th>
<th>( \Delta S^\circ )</th>
<th>( \Delta H^\circ /R )</th>
<th>( \Delta H^\circ ) ( \text{(kJ} \cdot \text{mol}^{-1}) )</th>
<th>( \Delta S^\circ ) ( \text{(J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>11.054</td>
<td>5240</td>
<td>43.56</td>
<td>-105.6</td>
</tr>
</tbody>
</table>

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_6]^{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 [PtCl₆]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:

\[
k_{obs} = kC_{reductant} + k'(20)
\]

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 \( [S_2O_3]^{2-} \) 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 kJ · mol⁻¹, and the increase of \( \Delta S^* \) from -129.5 to -105.6 J · mol⁻¹ · 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 [PtCl₆]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 [PtCl₆]²⁻ + Na₂S₂O₃. 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 ([PtCl₆]²⁻ and hydrolyzed species, e.g. [PtCl₅OH]⁻) can take part in the redox reaction with only one form of reductant ([S₂O₅]⁻).
- The suggested mechanism of the reaction in neutral solutions (pH = 7), can be described by the bimolecular reaction:

\[
^{+4}[PtCl_6]^{2-} + [S_2O_3]^{2-} \overset{k_1}{\rightarrow} [PtCl_4]^{2-} + [S_2O_4]^{2-} + 2H^+ + 2Cl^{-}
\]

- 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:

\[
^{+4}[PtCl_6]^{2-} + [S_2O_3]^{2-} \overset{k_2}{\rightarrow} [PtCl_4]^{2-} + [S_2O_4]^{2-} + 2H^+ + 2Cl^{-}
\]

\[
^{+4}[PtCl_6]^{2-} + OH^- \overset{k_3}{\rightarrow} [PtCl_5OH]^{2-} + Cl^{-}
\]

- The integral form of the rate equation for the studied reaction can be given in the form:
  - in neutral solution:
    \[ C_{[PtCl_6]} = C_{0}[PtCl_6]^{2-} \exp(-k_{obs}t) \] (values of \( k_{obs} \) at 25°C are given in the Table 2-4)
  - in alkaline solution:
    \[ C_{[PtCl_6]} = C_{0}[PtCl_6]^{2-} \exp\left(-k_{obs}T_{d(11054-520+1)}\right) \] (values of \( k_{obs} \) at 25°C are given in the Table 2-4)

- The order of reaction with respect to Pt(IV) ions in neutral solution is equal to “1”.

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