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CHEMICAL REDUCTION OF GOLD(III) BROMIDE COMPLEXES USING SODIUM NITRITE – KINETIC ASPECTS

In this work, the spectrophotometric studies on the kinetics of redox reaction between gold(III) bromide complexes and sodium nitrite, were carried out. From the kinetic curves collected under different conditions of reactants concentration, addition of bromide ions, temperature, pH and ionic strength, corresponding rate constants have been determined. The obtained results suggest the complex path of the $[\text{AuBr}_4]^-$ reduction consisting of two parallel, bimolecular reactions where different reductant species (HNO_2 and NO_2^-) take place and consecutive step with the metallic gold production. The second-order rate constants at 20°C are equal to 2.948 and 0.191 $\text{M}^{-1}\cdot\text{s}^{-1}$, respectively. The values of activation enthalpy and activation entropy for the first and the second parallel step of the reaction were found to be $\Delta H^\ddagger = 29.18 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -13.95 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}$, and $\Delta H^\ddagger = 40.75 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -31.06 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}$, respectively. It was found that the reaction accelerates significantly with the increase of pH and is inhibited with the increase of Br^- concentration. The substitutive, inner-sphere mechanism of electron transfer in the studied system was also suggested.

Keyword: Kinetics, Mechanism, Redox, Gold complexes, Sodium nitrite

1. Introduction

One of the effective leaching agent for gold recovery from solid wastes is the so-called “bromine water”, the mixture of H_2O and gaseous Br_2 , with addition of bromide ions [1-4]. The oxidative gold leaching carried out in such a system allows us to obtain an aqueous solution containing square-planar gold(III) bromide complexes [5] from which metallic gold can be potentially recovered in the form of powder. It can be performed e.g. using the chemical reduction [6-8], electro-reduction [9-11] or cementation [12-14]. The positive value of the standard oxidation-reduction potential of $[\text{AuBr}_4]^-/\text{Au}$ half-cell ($E^\circ = +0,854 \text{ V}$ [15]) indicates that potential reducing agent for gold(III) bromide complexes can be, among others, nitrite ($E^\circ_{[\text{NO}_2]^-/[\text{NO}_3]^-} = -0.940 \text{ V}$ [16]).

In the past, Gusev et al. [17] described the results of potassium nitrite application as a reductant of gold(III) chloride complexes. The authors, concluded redox character of the reaction from the bending on the thermometric titration curve. They also suggested the Au(II) and Au(I) complex formation as intermediates before the metallic gold formation in the studied system. However, the reaction took place in an aqueous solution containing Cl^- as ligands, not Br^- . It is worth noting that in the last few decades bromide system became alternative for the

chloride one especially for small refineries producing gold and platinum group metals using reduction methods. However, until now there is no kinetic studies of gold(III) bromide complexes reaction with nitrite, acting as a reducing agent. The kinetic data are preliminary to understanding the path of the reaction and partly the mechanism of electron transfer during the redox process. The results also give the chance to optimize the conditions for effective and efficient gold powder production in such a system. Therefore, the aim of this work was the kinetics study of $[\text{AuBr}_4]^-$ reaction with NaNO_2 in an aqueous solution under various conditions of reactants concentration, Br^- concentration, temperature and pH as well as proposition of the path and mechanism of the studied redox reaction.

2. Materials and methods

The stock solution of the gold(III) bromide complexes (used as precursor) was 19.3 mM tetrabromoauric acid (HAuBr_4). The pH range of an aqueous solution where the gold(III) bromide complex ($[\text{AuBr}_4]^-$) exists was experimentally determined by spectrophotometric titration using 0.1 M NaOH (until bands characteristic for this complex disappeared).

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Solutions containing precursor for all individual experiments were freshly prepared by appropriate dilution of the stock solution in 0.01 M HClO₄. The reductant solution was prepared by dissolving of appropriate analytical weight of the sodium nitrite (NaNO₂) powder in 0.01 M HClO₄. The Br⁻ concentration and ionic strength in the solutions were adjusted using NaBr and NaClO₄, respectively. All reactants were of analytical grade.

The kinetics of the reaction was measured spectrophotometrically (Shimadzu PC 2500 spectrophotometer, Kyoto, Japan) in several variants described in Table 1, under fixed, external conditions, i.e.: precursor concentration, reducing agent concentration, temperature, ionic strength, bromide ion concentration and pH. To initiate the reaction, reactants were mixed in a quartz cuvette in a volume ratio of 1:1. The cuvette containing reacting solutions was placed in a thermostated chamber of the spectrophotometer and then kinetic curves (change of absorbance value at 254 nm as a function of time) were recorded. The collected data were analyzed using TC Curve 2.0 software [18] to fit the

proper kinetic equation and to determine the value of reaction rate constants. The analysis of the chemical composition of gold precipitates were performed using XRF method (MiniPal 4, PANalytical, United Kingdom).

3. Results and discussion

3.1. Predominance diagrams of reactants

The equilibrium forms of expected reactants (gold(III) and nitrate(III)) in aqueous solution were predicted as a function of pH from the calculations using literature data [19] and [20], respectively. The diagrams shown in Fig. 1a and 1b represent the results of these calculations. They demonstrate that for pH ≤ 2 practically only one form of gold(III) and two forms of nitrite in aqueous solution may exist.

TABLE 1

Experimental variants and conditions under which kinetics of the reaction of gold(III) bromide complexes with sodium nitrite were carried out

Initial precursor concentration C_{HAuBr_4} , [mM]	Initial reductant concentration C_{NaNO_2} , [mM]	Temperature T , [K]	Ionic strength I , [mM]	Concentration of Br ⁻ C_{Br^-} , [mM]	pH
Effect of reductant concentration					
0.20	2.0	293	100	—	2.0
	3.0				
	4.0				
	5.0				
	6.0				
Effect of precursor concentration					
0.15	3.0	293	100	—	2.0
0.20	4.0				
0.25	5.0				
0.30	6.0				
0.35	7.0				
Effect of temperature					
0.20	4.0	285	100	—	2.0
		293			
		298			
		303			
		308			
Effect of ionic strength					
0.20	4.0	293	20	—	2.0
			40		
			60		
			80		
			100		
Effect of Br⁻					
0.20	4.0	293	100	0.2	2.0
				0.4	
				0.6	
				0.8	
				1.0	
Effect of pH solution					
0.20	4.0	293	100	—	1.0
					1.5
					2.0
					2.5
					3.0

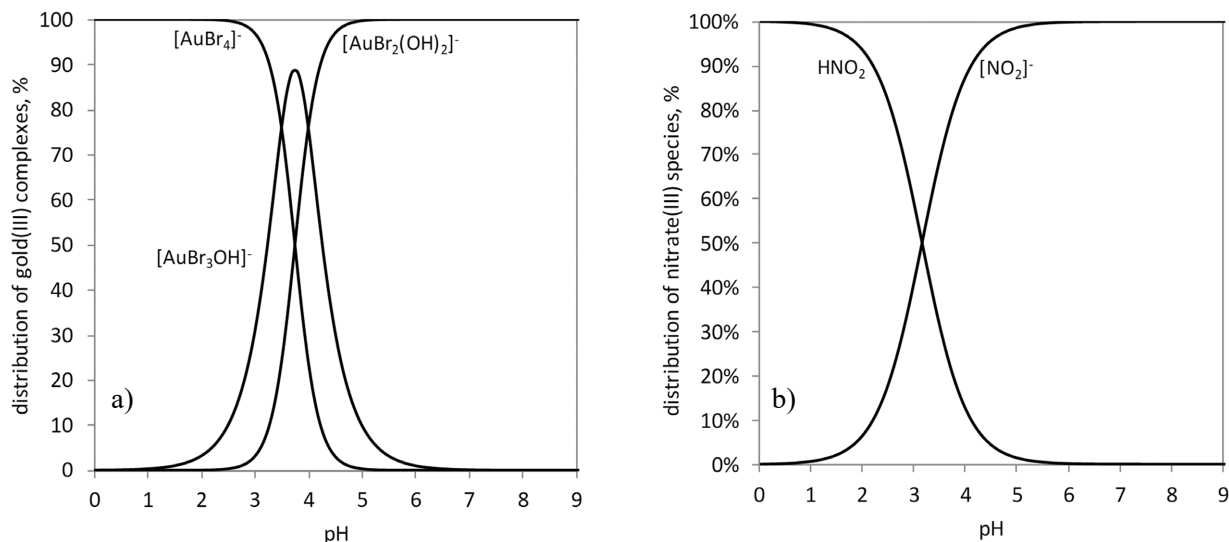
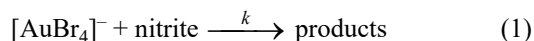


Fig. 1. Predominance diagrams of the equilibrium reactants species in aqueous solution at 25°C, as a function of pH: for gold(III) bromide complexes (a) and for nitrites (b) – calculated using data from [19] and [20], respectively.

3.2. Spectra of solutions

In the range of wavelength 190-900 nm, the spectra of the reactants before the reaction show the absorption bands with maximum at 254, 380 and 450 nm (Fig. 2a) which correspond well to the $[\text{AuBr}_4]^-$ [21] and the series of maxima in the range from ca. 320 to 380 nm, characteristic for nitrite [22].

It can be seen from Fig. 2b that bands intensities decrease after mixing of the reactants. This fact demonstrates the reaction progress between $[\text{AuBr}_4]^-$ and nitrite, which can be schematically described as:



Consequently, further kinetics measurements were made at the wavelength $\lambda = 254$ nm. The fitting procedure using TC-Curve software indicates the complex character of this reaction, confirmed by the form of the fitted equation:

$$y = a \exp(-k_1 t) + b \exp(-k_2 t) \quad (2)$$

This equation strongly suggests the existence of two parallel reactions (both of the first-order) during the step of gold(III) reduction. In general, such a mechanism is in agreement with the composition of the reactants solutions at $\text{pH} = 2.0$ predicted by predominance diagrams shown in Fig. 1a and 1b. From their analysis one can assume that two forms of reductant (HNO_2 and $[\text{NO}_2]^-$) and only one form of gold(III) ($[\text{AuBr}_4]^-$) predominate

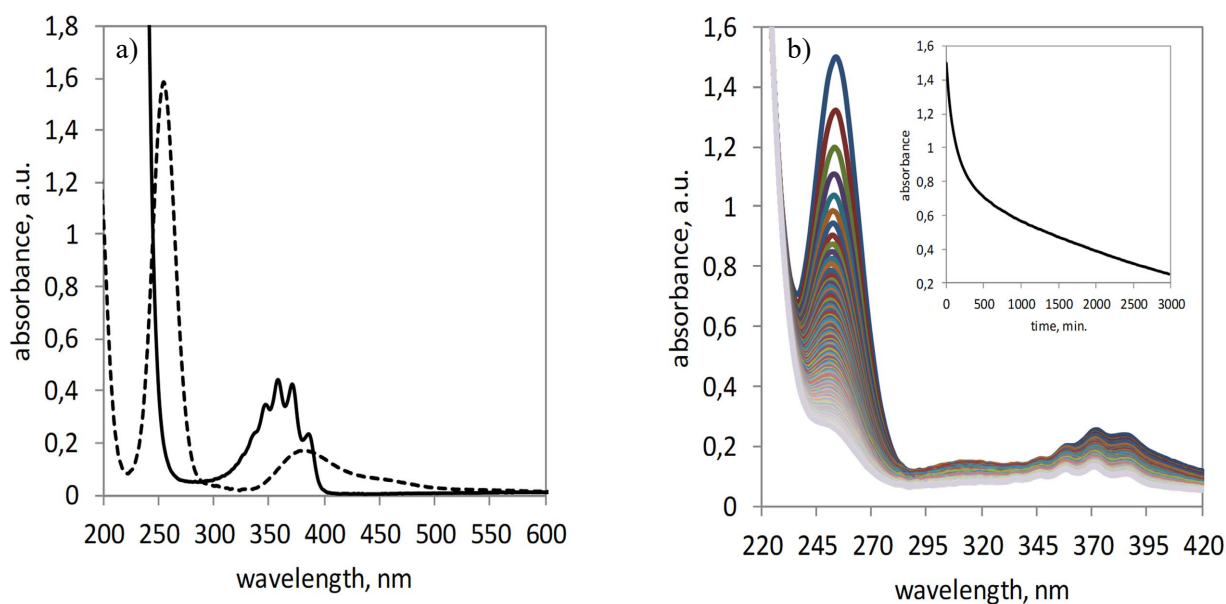
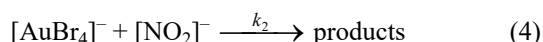
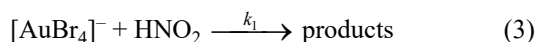


Fig. 2. Spectra of solutions containing the reactants with the absorption bands characteristic of gold(III) bromide complexes (dashed line) and sodium nitrite (solid line) – (a) and spectra of solution after mixing of reactants with the example of kinetic curve obtained at 254 nm (internal figure) – (b). Conditions: for a) $C_{[\text{AuBr}_4]^-} = 1.5 \cdot 10^{-4}$ M, $C_{\text{NaNO}_2} = 1 \cdot 10^{-2}$ M, $\text{pH} = 2.0$, $I = 0.10$ M NaClO_4 , temperature 20°C; for b) $C_{[\text{AuBr}_4]^-} = 2 \cdot 10^{-4}$ M, $C_{\text{NaNO}_2} = 4 \cdot 10^{-3}$ M, $\text{pH} = 2.0$, temperature 20°C

in the system, in such conditions. Consequently, two following reactions can be suggested:



3.3. Effect of reductant concentration

The kinetics of $[\text{AuBr}_4]^-$ decay for the parallel elementary reactions (3) and (4) is described by the rate equation:

$$-\frac{dC_{[\text{AuBr}_4]^-}}{dt} = k_1 C_{[\text{AuBr}_4]^-} C_{\text{HNO}_2} + k_2 C_{[\text{AuBr}_4]^-} C_{\text{NO}_2^-} \quad (5)$$

Under isolation conditions of the precursor (large excess of reductant with respect to the precursor) equation (5) can be transformed to the form:

$$-\frac{dC_{[\text{AuBr}_4]^-}}{dt} = k_{obs} C_{[\text{AuBr}_4]^-} \quad (6)$$

where:

$$k_{obs} = k_1 C_{\text{HNO}_2} + k_2 C_{\text{NO}_2^-} \quad (7)$$

or more symbolically:

$$k_{obs} = k_{obs,1} + k_{obs,2} \quad (8)$$

with:

$$k_{obs,1} = k_1 C_{\text{HNO}_2} \quad (9)$$

$$k_{obs,2} = k_2 C_{\text{NO}_2^-} \quad (10)$$

To verify the dependences (9) and (10), the effect of reductant concentration on the kinetics of the reaction was investigated. These relationships are helpful to determine the molecularity of suggested $[\text{AuBr}_4]^-$ reduction steps. All measurements were carried out at increasing concentration of the reductant (from 2 to 6 mM). The values of the rate constants determined from kinetic curves under these conditions, and the $k_{obs,1} = f(C_{\text{NaNO}_2})$ as well as the $k_{obs,2} = f(C_{\text{NaNO}_2})$ dependences are shown in Table 2 and Fig. 3, respectively.

TABLE 2

The rate constants of the reaction, $k_{obs,1}$ and $k_{obs,2}$, determined at different reductant concentration.
Conditions: $C_{[\text{AuBr}_4]^-} = 2.0 \cdot 10^{-4}$ M, $C_{\text{NaNO}_2} = 2.6 \cdot 10^{-3}$ M, pH = 2.0, $I = 0.10$ M NaClO₄, temperature 20°C

The reductant concentration, C_{NaNO_2} mM	$k_{obs,1} \cdot 10^3, \text{ s}^{-1}$	$k_{obs,2} \cdot 10^3, \text{ s}^{-1}$	$k_1 \cdot 10^3, \text{ M}^{-1}\text{s}^{-1}$	$k_2 \cdot 10^3, \text{ M}^{-1}\text{s}^{-1}$
2.0	5.28	0.26	2.82	1.96
4.0	8.28	0.37	2.22	1.40
6.0	11.8	0.71	2.11	1.79
8.0	13.5	0.97	1.81	1.84
10.0	19.2	1.31	2.05	1.98

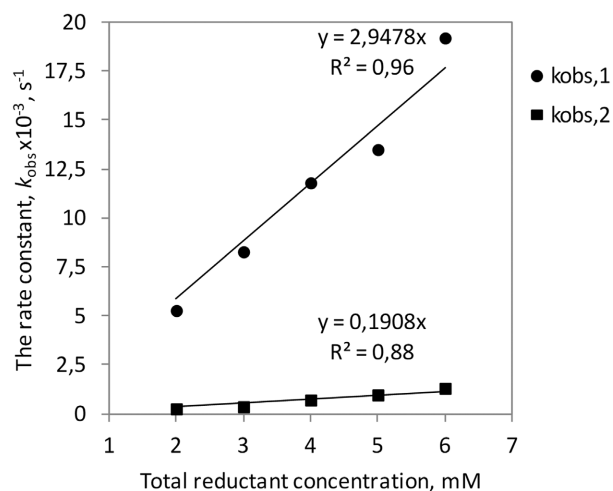


Fig. 3. The relationship of $k_{obs,1}$ and $k_{obs,2}$ vs. reductant concentration in the reaction of $[\text{AuBr}_4]^-$ with NaNO_2 . Conditions: $C_{[\text{AuBr}_4]^-} = 2.0 \cdot 10^{-4}$ M, $C_{\text{NaNO}_2} = 2.6 \cdot 10^{-3}$ M, pH = 2.0, $I = 0.10$ M NaClO₄, temperature 20°C

The obtained empirical equations:

$$k_{obs,1} = 2.948 \cdot C_{\text{nitrite}} \quad (11)$$

$$k_{obs,2} = 0.191 \cdot C_{\text{nitrite}} \quad (12)$$

confirm the existence of two parallel, bimolecular reactions. Thus, one can assume that obtained experimental results confirm the complex model of reduction reaction, described by eq. (3) and (4).

3.4. Effect of precursor concentration

To determine the order of the reaction with respect to gold(III) bromide complex concentration, the initial rate method was used [23]. All measurements were performed for different concentrations of $[\text{AuBr}_4]^-$, and at constant excess of the reductant concentration. Detailed conditions and obtained values of $k_{obs,1}$ and $k_{obs,2}$ are gathered in Table 4.

TABLE 4

The rate constants of the reaction, $k_{obs,1}$ and $k_{obs,2}$, determined at different initial concentrations of precursor ($[\text{AuBr}_4]^-$). Conditions: temperature 20°C, pH = 2, $I = 0.10$ M NaClO₄

Initial concentration of precursor, $C_{0,[\text{AuBr}_4]^-} \cdot 10^4$ M	The observed rate constant $k_{obs,1} \cdot 10^3, \text{ s}^{-1}$	The observed rate constant $k_{obs,2} \cdot 10^3, \text{ s}^{-1}$
1.5	6.70	0.44
1.0	11.8	0.71
2.5	12.6	0.79
3.0	15.5	0.99
3.5	21.7	1.02

Assuming that the initial rate of elementary reaction (V_0) is the function of gold(III) initial concentration:

$$V_0 = k_{obs} C_{0,[\text{AuBr}_4]^-}^\alpha \quad (13)$$

where α is the order of the reaction with respect to $[\text{AuBr}_4]^-$ ions, the linear form of equation (13) can be obtained:

$$\log V_0 = \log k_{obs} + \alpha \log C_{0,[\text{AuBr}_4]^-} \quad (14)$$

Experimental relationship determined for rate constants $k_{obs,1}$ and $k_{obs,2}$ using eq. (14) is shown in Fig. 4.

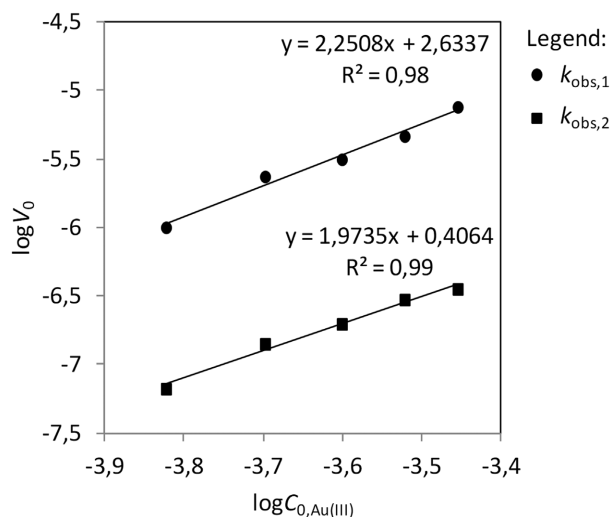


Fig. 4. Dependence of $\log(V_0)$ vs. $\log(C_{\text{Au(III)},0})$ – the slope determines the order of reaction with respect to gold(III) complexes. Conditions: $\text{pH} = 2.0$, $I = 0.10 \text{ M NaClO}_4$, temperature 20°C

From these data we can deduce, that the form of kinetic equation contains the gold(III) concentration in the power of 2. This fact indicates for more complex character of the reaction path and faster disappearance of gold(III) in the solution than predicted by fitting rate equation (2).

3.5. Effect of temperature

The effect of temperature on the reaction rate constant was studied to determine the activation parameters in Eyring equation. The kinetics of the reaction was measured at 15, 20, 25, 30 and 35°C . Experimentally determined values of the rate constants are gathered in Table 5.

Using data from Table 6 and the linear form of Eyring dependence (eq. 15), the values of enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) of activation were determined graphically (Fig. 5):

$$\ln\left(\frac{k_{obs}}{T}\right) = 23.759 + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (15)$$

3.6. Effect of ionic strength

To determine the effect of ionic strength (I) on the rate constant of the reaction, the kinetics measurements were carried out under different NaClO_4 concentrations: 0.02; 0.04; 0.06; 0.08 and 0.1 M. Determined values of the reaction rate constants are shown in Table 7.

TABLE 5

The observed rate constants of redox reaction of the gold(III) bromide complexes with sodium nitrite obtained at different temperatures. Conditions: $C_{[\text{AuBr}_4]^-} = 2 \cdot 10^{-4} \text{ M}$, $C_{\text{NaNO}_2} = 4 \cdot 10^{-3} \text{ M}$, $\text{pH} = 2.0$

Temperature, $^\circ\text{C}$	$k_{obs,1} \cdot 10^3, \text{ s}^{-1}$	$k_{obs,2} \cdot 10^3, \text{ s}^{-1}$
15	6.9	0.48
20	11.8	0.71
25	12.8	0.83
30	15.9	1.29
35	17.3	1.54

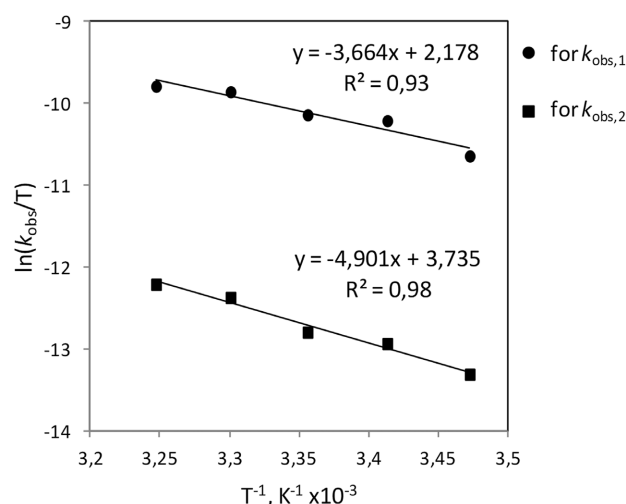


Fig. 5. Eyring dependence for the reaction of $[\text{AuBr}_4]^-$ with sodium nitrite obtained from $k_{obs,1}$ and $k_{obs,2}$ data. Conditions: $C_{[\text{AuBr}_4]^-} = 2 \cdot 10^{-4} \text{ M}$, $C_{\text{NaNO}_2} = 4 \cdot 10^{-3} \text{ M}$, $\text{pH} = 2.0$, $I = 0.10 \text{ M NaClO}_4$

TABLE 6

The activation parameters in Eyring equation for the reaction of gold(III) bromide complexes with sodium nitrite

Reaction	$\Delta H^\ddagger, \text{ kJ} \cdot \text{mol}^{-1}$	$\Delta S^\ddagger, \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
The reaction step described by $k_{obs,1}$	29.18	-13.95
The reaction step described by $k_{obs,2}$	40.75	-31.06

TABLE 7

The rate constants ($k_{obs,1}$ and $k_{obs,2}$) of reaction between gold(III) bromide complexes and sodium nitrite at different ionic strength. Conditions: $C_{[\text{AuBr}_4]^-} = 2 \cdot 10^{-4} \text{ M}$, $C_{\text{NaNO}_2} = 4 \cdot 10^{-3} \text{ M}$, $\text{pH} = 2.0$, temperature 20°C

Sila jonowa, $I \text{ M}$	$k_{obs,1} \cdot 10^3, \text{ s}^{-1}$	$k_{obs,2} \cdot 10^3, \text{ s}^{-1}$
0.02	2.35	0.45
0.04	2.51	0.46
0.06	4.30	0.49
0.08	4.33	0.61
0.10	6.02	0.55

Using the Brönsted-Bjerrum (B-B) equation:

$$\log \left(\frac{k_{obs}(I)}{k_{obs}(0)} \right) = 2z_A z_B A \frac{\sqrt{I}}{1 + \sqrt{I}} \quad (16)$$

where $z_A \equiv z_{Au(III)}$, $z_B \equiv z_{nitrite}$ are the charges of reactants, A is a constant (for aqueous solutions at 25°C, $A = 0.51$) and using the rate constants from Table 7, the $\log \left(\frac{k_{obs}(I)}{k_{obs}(0)} \right) = f \left(\frac{\sqrt{I}}{1 + \sqrt{I}} \right)$ dependence was calculated and is shown in Fig. 6.

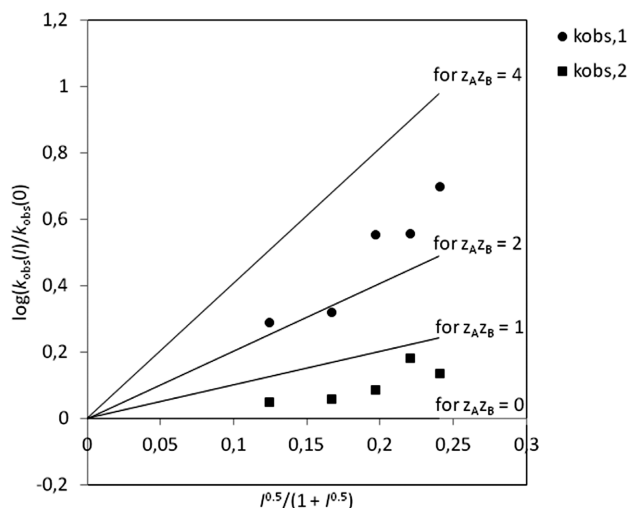


Fig. 6. The Brönsted-Bjerrum dependence determined using the rate constants ($k_{obs,1}$ and $k_{obs,2}$) of the $[AuBr_4]^-$ with $NaNO_2$ reaction. Conditions: $C_{[AuBr_4]^-} = 2 \cdot 10^{-4}$ M, $C_{NaNO_2} = 4 \cdot 10^{-3}$ M, pH = 2.0, temperature 20°C

Analyzing experimental data shown in Fig. 6, it can be concluded that the product of charges of reacting species ($z_{A(III)}$, $z_{nitrite}$) in B-B equation is positive in case of $k_{obs,1}$ and oscillates between “0” and “+1” model in case of $k_{obs,2}$. Taking into account these results as well as negative charge of the precursor ($[AuBr_4]^-$), the species reacting with gold(III) correspond closely to the charged ($[NO_2]^-$) and neutral (HNO_2) form of the nitrite. It is also in good agreement with the contribution of these species at pH = 2, visible on predominance diagram (Fig. 1b).

3.7. Effect of Br^- concentration

The addition of halide ions, which are potential ligands of gold complexes, to the solution may cause changes in the redox reaction rate in which these complexes are involved. For example, the presence of Cl^- ions in the reaction environment of gold(III) chloride complexes with various reducing agents inhibits these reactions [24,25]. It seems that, by analogy with chloride systems, bromide ions can also inhibit the progress of the reduction reaction. Therefore, the goal was to determine the impact of the Br^- ions in the system on the rate of $[AuBr_4]^-$ reduction reaction. The kinetics were measured at various concentrations of NaBr in solution. Experimentally determined the reaction rate constants are given in Table 8.

TABLE 8

The rate constants ($k_{obs,1}$ and $k_{obs,2}$) of reaction between $[AuBr_4]^-$ and $NaNO_2$, obtained at different concentration of Br^- ions. Conditions: $C_{[AuBr_4]^-} = 2 \cdot 10^{-4}$ M, $C_{NaNO_2} = 4 \cdot 10^{-3}$ M, pH = 2.0, temperature 20°C

Br^- concentration C_{NaBr} mM	$k_{obs,1} \cdot 10^3$, s^{-1}	$k_{obs,2} \cdot 10^3$, s^{-1}
0.2	5.6	0.82
0.4	5.0	0.78
0.6	4.6	0.71
0.8	4.1	0.65
1.0	3.9	0.59

The bromide ions addition results in decrease of the rate constants value $k_{obs,1}$ and $k_{obs,2}$ (Fig. 7). These trends are described by equations:

$$k_{obs,1} = -2.15C_{Br^-} + 5.93 \quad (17)$$

$$k_{obs,2} = -0.295C_{Br^-} + 0.885 \quad (18)$$

Inhibiting effect of Br^- on the reaction rate may indicate a mechanism involving the ligand substitution by nitrite prior to electron transfer between the reactants. Bromide ions “shielding” the complex of gold(III) may result in a steric hindrance which inhibits the Br^- ligand substitution by the species of reductant.

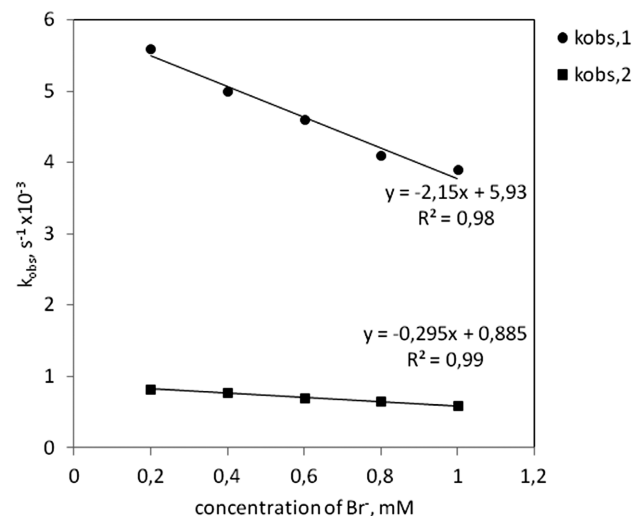


Fig. 7. The dependence of the rate constant ($k_{obs,1}$ and $k_{obs,2}$) on Br^- concentration for reaction of bromide gold(III) complexes with sodium nitrate(III). Conditions: $C_{[AuBr_4]^-} = 2 \cdot 10^{-4}$ M, $C_{NaNO_2} = 4 \cdot 10^{-3}$ M, pH = 2.0, temperature 20°C

3.8. Effect of pH

The pH effect on the reaction kinetics was measured in solutions with a pH equal to: 1.0; 1.3; 2.0; 2.3 and 3.0. Experimentally determined rate constants ($k_{obs,1}$ and $k_{obs,2}$) are shown in Table 9.

The influence of pH on the rate constant of the reaction is shown in Fig. 8. In both cases, the value of $k_{obs,1}$ and $k_{obs,2}$

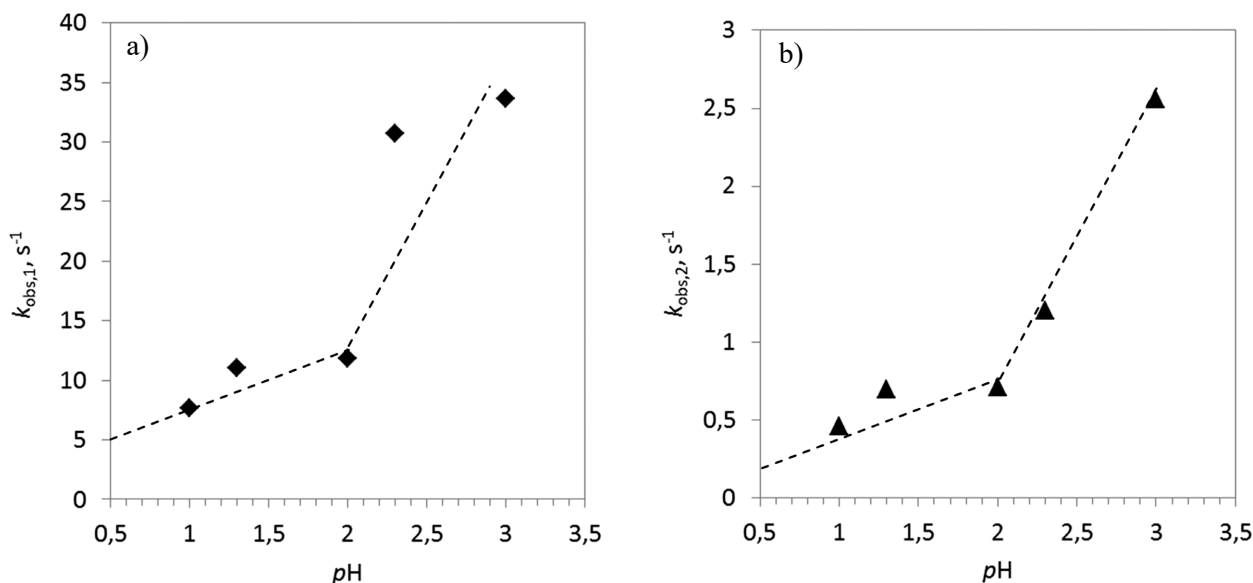


Fig. 8. The influence of pH on the rate constants ($k_{\text{obs},1}$ and $k_{\text{obs},2}$) of the reaction between $[\text{AuBr}_4]^-$ and NaNO_2 . Conditions: $C_{[\text{AuBr}_4]^-} = 2 \cdot 10^{-4}$ M, $C_{\text{NaNO}_2} = 4 \cdot 10^{-3}$ M, temperature 20°C, pH = 2.0

increase with the increase of pH. It can be also seen, that these relationships are not linear – in the range of pH from 2 to 3 the slopes change rapidly.

TABLE 9

The values of the rate constants $k_{\text{obs},1}$ and $k_{\text{obs},2}$ obtained at different pH conditions in solution. Conditions: $C_{[\text{AuBr}_4]^-} = 2 \cdot 10^{-4}$ M, $C_{\text{NaNO}_2} = 4 \cdot 10^{-3}$ M, pH = 2.0, temperature 20°C

pH	$k_{\text{obs},1} \cdot 10^3, \text{ s}^{-1}$	$k_{\text{obs},2} \cdot 10^3, \text{ s}^{-1}$
1.0	7.71	0.46
1.3	11.0	0.70
2.0	11.8	0.71
2.3	30.7	1.20
3.0	33.6	2.56

Analysing the predominance diagram of the equilibrium species of the reductant (Fig. 1b) it is clearly seen that the rapid increase of the rate constants, beginning from pH = 2, correlates well with the increase of the $[\text{NO}_2]^-$ contribution in reductant solution. It can be concluded that the ionized form of nitrite shows higher reactivity than its molecular analogue (HNO_2). A similar effect was noticed in the redox reaction of gold(III) chloride complexes with sulfate(IV) applied as reducing agent [25]. The increase of the rate constant with pH may indicate the inner-sphere character of electron transfer in the redox reaction, preceded by substitution of Br^- ligand in the square-planar gold(III) complex with the ionic form of reductant. The analogical mechanism (ligand substitution by $[\text{NO}_2]^-$ in Au(III) and Pt(II) square-planar complexes) was described by the Catalini *at al.* [26], confirmed in the spectrophotometric studies. This type of charge transfer causes usually in faster electron transfer.

3.9. Metallic gold formation

After increasing of initial gold(III) concentration to 0.01 M in the system, the reaction of gold(III) bromide complexes with nitrite leads to the metallic phase of gold formation. The reactions carried out under different pH conditions (1, 2, 3 and 4), in all cases resulted in gold powder formation. The chemical composition of the metallic product appeared in the solution was determined using XRF method (Fig. 9a-c). It can be seen that in each case, the pure metallic gold was formed. Assuming that intensity of registered spectra for the samples is proportional to the efficiency (Ef) of the gold precipitation, one can estimate that Ef of the process increases with the increase of pH value. The differences between samples can be described as a multiple of a base value (intensity at pH = 1 which was taken as 1), which for the increasing pH in the solution from 1 to 4 gives a series: 1 : 2 : 5 : 15.

4. Conclusions

1. The kinetic equation fitted to the experimental data indicates the complex path of the reduction of gold(III) bromide complexes. In the first stage two parallel reactions take place in which $[\text{AuBr}_4]^-$ is reduced by molecular (HNO_2) and ionized ($[\text{NO}_2]^-$) form of the reductant.
2. The dependences of the reaction rate constants ($k_{\text{obs},1}$ and $k_{\text{obs},2}$) vs. sodium nitrite concentration are linear indicating that both stages of gold(III) ions reduction follows by bimolecular collision mechanism. Corresponding second-order rate constants, k_1 and k_2 , of these stages are equal to 2.948 and 0,191 $\text{M}^{-1} \cdot \text{s}^{-1}$, respectively.
3. The order of the redox reaction with respect to $[\text{AuBr}_4]^-$ for both parallel steps is equal to 2. This fact indicates the

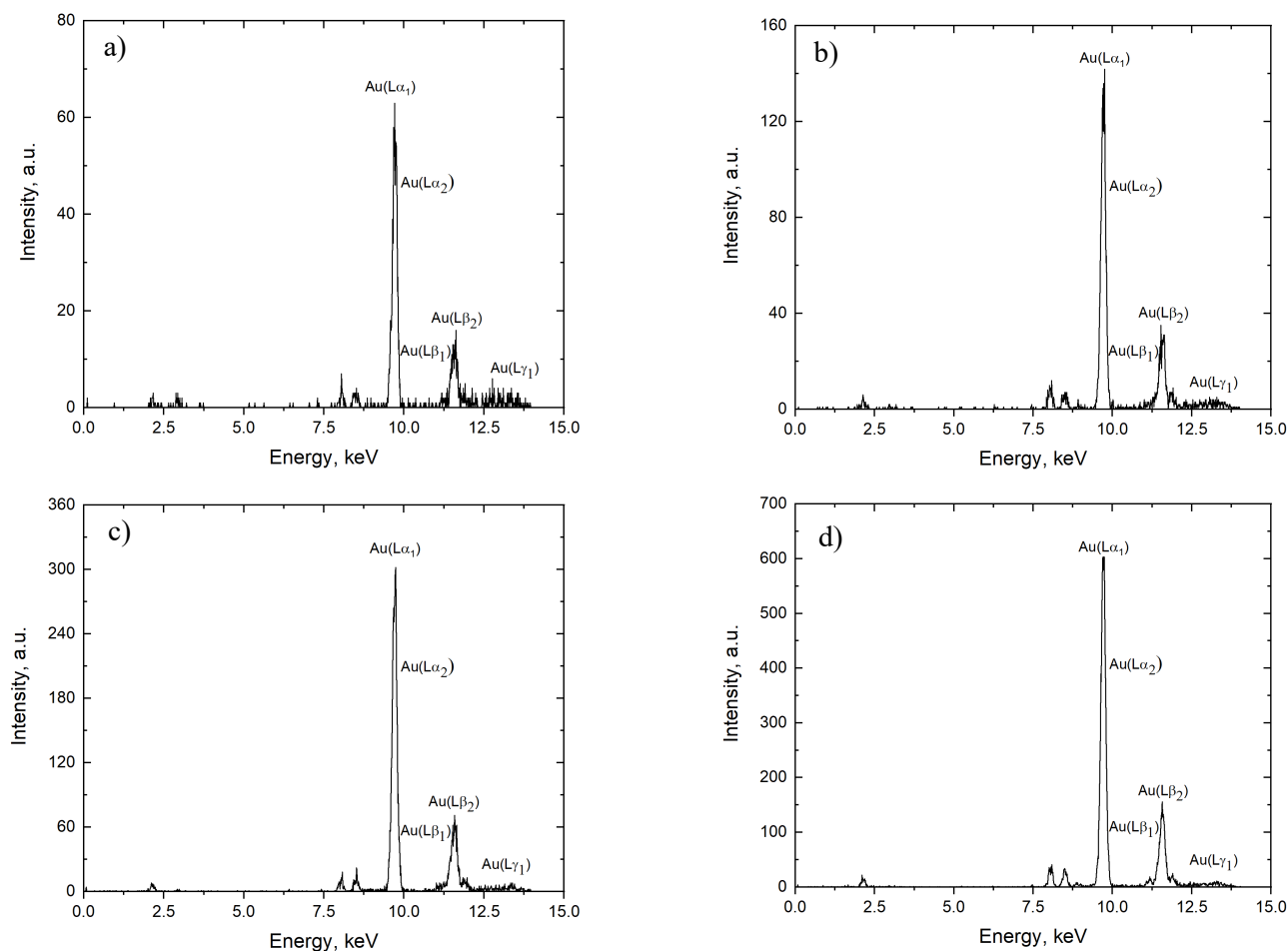


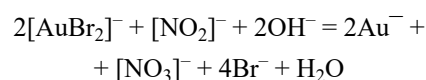
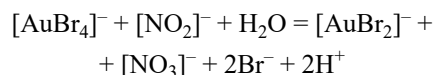
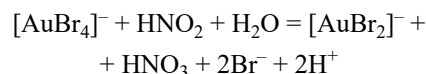
Fig. 9. The XRF spectra of the metallic phase of gold as a product of gold(III) bromide complexes reduction using sodium nitrite, at pH: 1 (a), 2 (b), 3 (c) and 5 (d)

complex nature of reduction stages and faster disappearance of gold(III) substrate in the system than predicted by the formula of fitted kinetic equation.

- The increase of temperature accelerates the reaction. In the range from 15 to 30°C, the reaction rate constants, k_1 and k_2 , fulfills the Eyring equation. The corresponding values of the activation parameters (enthalpy and entropy of activation) are as follows: for the reaction of $[\text{AuBr}_4]^-$ with HNO_2 the $\Delta H^\ddagger = 40.75 \text{ kJ/mol}$ and the $\Delta S^\ddagger = -31.06 \text{ J/K}\cdot\text{mol}$; for the reaction of $[\text{AuBr}_4]^-$ with $[\text{NO}_2]^-$ the $\Delta H^\ddagger = 29.18 \text{ kJ/mol}$ and the $\Delta S^\ddagger = -13.95 \text{ J/K}\cdot\text{mol}$.
- The increase of ionic strength (I) of the solution from 0.02 to 0.1 M causes the increase of the $k_{\text{obs},1}$ rate constant value (from $2.35 \cdot 10^{-3}$ to $6.02 \cdot 10^{-3} \text{ s}^{-1}$) and does not cause significant change in the $k_{\text{obs},2}$ value (average value: $2.56 \cdot 10^{-3} \text{ s}^{-1}$). The charges of reductant species estimated from the Brønsted-Bjerrum relation confirm the reaction of $[\text{AuBr}_4]^-$ with the negatively charged species and the uncharged one. It corresponds well to the $[\text{NO}_2]^-$ anion and protonated form of nitrite (HNO_2) as electron donors.
- An increase of pH from 2 to 3 in the solution causes an increase of the reaction rate constant value: from $7.71 \cdot 10^{-3}$ to $33.6 \cdot 10^{-3} \text{ s}^{-1}$ for $k_{\text{obs},1}$ and $0.46 \cdot 10^{-3}$ to $2.56 \cdot 10^{-3} \text{ s}^{-1}$ for $k_{\text{obs},2}$, respectively. These changes are caused

by the higher contribution of more reactive, ionized form of nitrite ($[\text{NO}_2]^-$) in the solution.

- The increase of Br^- concentration in the solution causes a decrease in the value of the rate constants $k_{\text{obs},1}$ and $k_{\text{obs},2}$. The inhibiting effect of Br^- on the reaction rate may indicate a substitutive, inner-sphere mechanism of electron transfer in the studied redox reaction.
- In the pH range from 1 to 4, the subsequent gold(I) bromide complex reduction reaction takes place with the gold metallic phase formation in the system. The change of efficiency of the gold precipitation under these conditions is significant and was estimated as a series: 1 : 2 : 5 : 15.
- Basing on the collected kinetic data as well as the spectral changes during the reaction, the following path of the redox reaction is suggested:



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