

A STUDY OF THE INTERACTION BETWEEN RHENIUM(VII)
AND ALLYLTHIOUREA BY SPECTROPHOTOMETRY

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The possibility to obtain a complex compound of the rhenium(V) with allylthiourea has been studied. The optimal conditions, in which the chemical reaction took place, have been estimated. It has been shown that this reaction may be used for spectrophotometric determination of rhenium(VII).

It has been approved by means of potentiometric titration method that 1 mol quantity of tin(II) chloride is necessary to reduce 1 mol quantity of perrhenate, which witnesses about the reducing of the Re(VII) to Re(V). Allylthiourea and Re(V) form a new yellow colored complex substance having maximal light absorption at $\lambda = 365 \text{ nm}$ wavelength.

Keywords: perrhenate, allylthiourea; rhenium(V)-allylthiourea complexes.

Introduction. The questions relating to the study of the chemical-analytical properties of rhenium and its quantitative determination were discussed in detail in some fundamental sources [1–3], where voluminous information was given on the chemical state of the rhenium in aqueous solutions, methods for its isolation and determination, as well as information connected to the methods for analysis of the rhenium-containing materials (alloys, ores, etc.).

The peculiarities of the rhenium chemistry in the solutions are connected with its ability to realize variety of oxidation states in its compounds: rhenium compounds may undergo hydrolysis, oxidation-reducing (particularly disproportionation). The most stable in aqueous solutions among them are Re(VII) and Re(IV) compounds.

One of the characteristic properties of the rhenium in lower oxidation states is its inclination to the complex formation inherent to all transition metals. When studying complex formation reactions the particular attention is spared to the search of optimal conditions for forming colored compounds, their stability, their composition and structure. When acting with Re(V) the thiourea derivatives form yellow-colored complex compounds having maximal light absorption at $\lambda = 365 \text{ nm}$ wavelength [3].

The synthesis of Re(V) complexes with several organic sulfur-containing ligands has been described later in [4–7]. A possibility of obtaining the complex of Re(V) with allylthiourea has been studied by us in the recent work.

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Experimental Part. Perrhenate spare solution with $1 \cdot 10^{-2} \text{ mol/L}$ concentration has been prepared by dissolution of the accurate weighed sample of KReO_4 in distilled water. The allylthiourea (ATU) solution with $1 \cdot 10^{-2} \text{ mol/L}$ concentration has been prepared by dissolution of the accurate weighed recrystallized preparation in distilled water. 10% solution of tin(II) chloride in diluted hydrochloric acid (1:1) has been used as a reducing agent, and the acidity of the reaction medium has been approved by addition proper volume of concentrated hydrochloric acid.

The method of potentiometric titration of perrhenate by standard solution of Sn(II) chloride has been applied for determination of oxidation state of rhenium in the experiment conditions ($2.0\text{--}5.0 \text{ mol/L}$ acidity by hydrochloric acid). Platinum has been used as an indicative electrode. The system potential was settled slowly and the titration jump was observed after addition of the accurately 1 mol reducing agent. It means that in the above mentioned conditions Re(VII) is reduced to Re(V) oxidation state (Fig. 1).

The Re(VII)– Sn(II)– ATU system has been studied by spectrophotometric method as well to confirm oxidation state of rhenium in the obtained compound (the colored compound has maximal absorption at 365 nm wavelength). For this purpose isomolar series of solutions has been prepared, where ATU concentration has been kept constant (surplus) and concentrations of Re(VII) and Sn(II) chloride was varied (the sum of concentrations was kept $5 \cdot 10^{-3} \text{ mol/L}$). The maximal light absorption was observed at Re(VII) : Sn(II) = 1 : 1 molar ratio, which corresponds to the reducing of Re(VII) to Re(V) (Fig. 2).

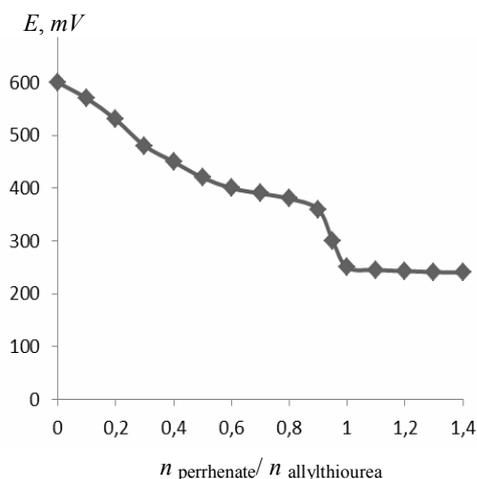


Fig. 1. Potentiometric titration of perrhenate by Sn(II) chloride:
 $[\text{ReO}_4^-] = 5 \cdot 10^{-3} \text{ mol/L}$;
 $[\text{ATU}] = 5 \cdot 10^{-3} \text{ mol/L}$.

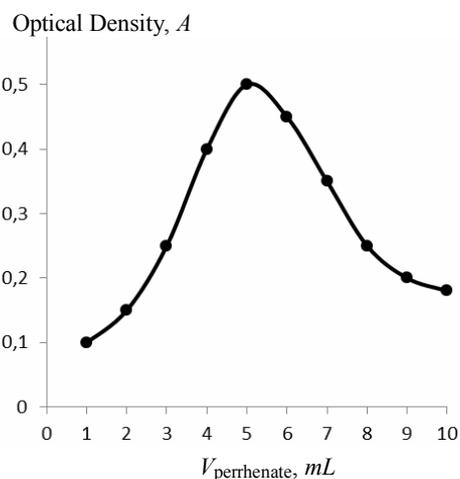


Fig. 2. Isomolar series of the Re(VII) and Sn(II) solutions (total concentration $5 \cdot 10^{-3} \text{ mol/L}$) in the presence of ATU:
 $V_{\text{Sn(II) chloride}} + V_{\text{perrhenate}} = 10.0 \text{ mL}$.

The study of the interaction of ATU with perrhenate in the presence and in absent of the reducing agent has been shown that the addition of the great surplus of the reagent to the potassium perrhenate acidic solutions leads to the formation of the yellow-colored complex compound. The maximal absorption is observed at the same wavelength 365 nm .

Inasmuch ATU possesses reducing properties one can assume that Re(VII) participates to the complex formation in lower oxidation state. The reaction proceeds slowly and it is expedient to introduce off-site reducing agent – Sn(II) chloride.

The saturation method has been used when studying the influence of tin(II) chloride concentration on the complex formation of rhenium with ATU. The solutions investigated contained constant concentration of rhenium(VII) ($5.0 \cdot 10^{-3} \text{ mol/L}$), ATU ($5.0 \cdot 10^{-3} \text{ mol/L}$) and variable concentration of tin(II) chloride. Acidity corresponds to 3.0 mol/L by hydrochloric acid and the volume of the solutions was kept constant (25 mL).

It has been ascertained that 20-fold surplus of the Sn(II) chloride is enough to assure complex formation of Re(VII) with ATU. Higher content of the reducing agent did not change optical density values of the system. The invariable maximal values had reached within $15\text{--}20 \text{ min}$ and then stay invariable during 24 h and even longer. Moderate heating of the system (up to 70°C) promotes faster development of the color ($5\text{--}7 \text{ min}$).

The order of the reagents addition also is important. The maximal coloring was secured in case when first requested amount of the hydrochloric acid was added to the perrhenate solution, then allylthiourea solution, and finally – the tin(II) chloride solution.

The colored Re(V)–ATU compound forms in hydrochloric acid media. Absorption spectra obtained in the presence of different concentration of hydrochloric acid showed that the maximal optical density for the forming compound is observed when acidity corresponds to $2.0\text{--}6.0 \text{ mol/L}$ by hydrochloric acid).

The saturation method (the method of continuous change of the reagent concentration) has been applied to estimate the required amount of ATU keeping the rhenium(VII) concentration constant ($1.0 \cdot 10^{-4} \text{ mol/L}$ and $2.0 \cdot 10^{-4} \text{ mol/L}$). The maximal coloring of the complex is developed already at three-fold molar surplus of the ATU. Further increase of the reagent concentration has no influence on the optical density values and it may witnesses that only a complex with one composition arose.

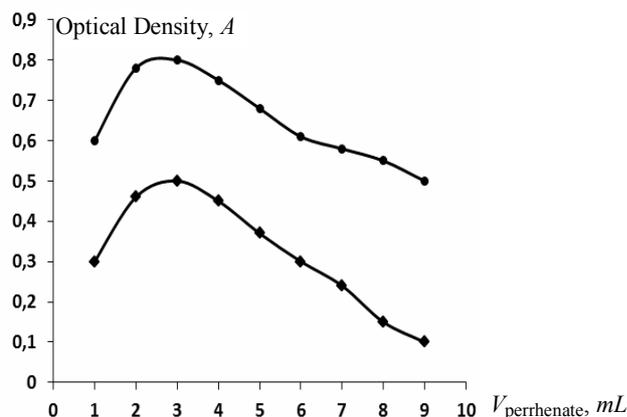
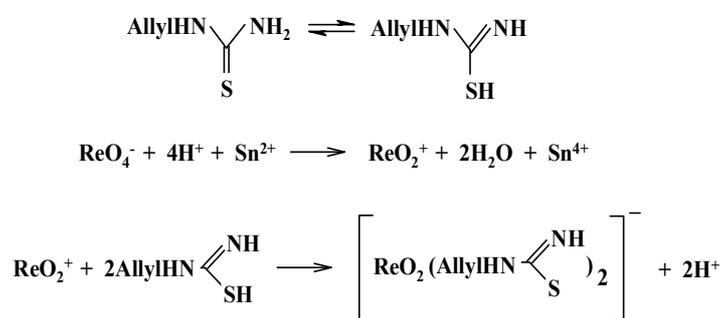


Fig. 3. Isomolar series of the solutions with total concentration rhenium(VII) and allylthiourea equals to $4 \cdot 10^{-4} \text{ mol/L}$ (1) and $8 \cdot 10^{-4} \text{ mol/L}$ (acidity – 3.0 mol/L by hydrochloric acid);
 $V_{\text{perrhenate}} + V_{\text{allylthiourea}} = 10.0 \text{ mL}$.

The isomolar series method indicates that molar ratio of the acting reagents in the forming compounds is as following $[\text{Re(VII)}] : [\text{ATU}] = 1 : 3$ (Fig. 3).

Calibration curve is linear for the Re(VII) contents within 0.8–8.0 mcg/mL range.

The molar extinction coefficient (ε) calculated according to the calibration curve data equals $3550 \text{ cm}\cdot\text{L}\cdot\text{mol}^{-1}$ at 365 nm wavelength. Insufficiently sharp maximum at the isomolar series curves may witnesses about partial dissociation of the obtained complex compound. We assume that the reaction proceeds according to the following Scheme:



When studying the interfering influence of several elements during the spectrophotometric measurements of the optical density of $\text{Re(V)}\text{--ATU}$ complex it has been revealed that molybdenum and tungsten may form similar complexes. That is these elements will interfere rhenium(VII) determination causing overestimated results. Under stated results have been obtained in the presence of mercury(II), bismuth(III). Selenium(IV) may be reduced to the elementary state (red precipitate), tellurium(IV) form yellow-colored compound. So, all mentioned elements interfere rhenium(VII) determination by ATU.

Conclusion. The presence of tin(II) chloride rhenium(VII) interact with ATU forming yellow-colored complex compound with maximal light absorption at $\lambda = 365 \text{ nm}$ wavelength. The optimal conditions for arising the complex compound have been revealed: 20-fold surplus amounts of the reducing agent (SnCl_2).

At least three-fold surplus of the reagent (ATU); medium acidity is 0.5–5.0 mol/L by hydrochloric acid; color development time is 20 min ; color is stable more than 24 h .

The molar ratio between reacting agents is following:



This fact has been confirmed by means of saturation and isomolar series methods.

Received 17.06.2014

REFERENCES

1. **Borisova L.V., Yermakov A.N.** Analytical Chemistry of Rhenium. M.: Nauka, 1974 (in Russian).

2. "Rhenium. Chemistry, Technologies, Analysis." Trudi Vsesoyuznogo Soveschaniya po Probleme Rheniya. M.: Nauka, 1976 (in Russian).
3. **Tarayan V.M.** Analytical Chemistry of Rhenium. Yer.: Mitk, 1966 (in Russian).
4. **Gagieva S.Ch., Tsaloev A.T., Gutnova N.A. et al.** Synthesis and Physical and Chemical Characteristics of the Rhenium(V) Coordinating Compounds with Thiocarbazon of Phenylglioksal Acids. // J. of Inorganic Chemistry, 2002, v. 47, № 5, p. 815–818 (in Russian).
5. **Gagieva S.Ch., Tsaloev A.T., Gutnova N.A. et al.** Synthesis and Physical and Chemical Characteristics of the Rhenium(V) Coordinating Compounds with Bis-Benzoilthiosemicarbazon. // J. of Inorganic Chemistry, 2003, v. 48, № 5, p. 776–781 (in Russian).
6. **Gagieva S.Ch., Tsaloev A.T., Gutnova N.A. et al.** Synthesis and Physical and Chemical Characteristics of the Rhenium(V) Coordinating Compounds with Mercaptobenzothiozol. // J. of Inorganic Chemistry, 2003, v. 48, № 2, p. 2034–2038 (in Russian).
7. **Aminjanov A.A., Safarmamadov S.M., Orifov A.A.** Rhenium(V) Complex Compounds with 2-Mercaptoimidazol. // J. of Inorganic Chemistry, 2005, v. 50, № 1, p. 49–53 (in Russian).