

Preparation of Binuclear Rhodium(II) Tetraacetate (Initial Compound for the Coulometric Determination of Rhodium) under the Action of Microwave Radiation

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Received January 28, 2000; in final form, March 28, 2000

Abstract—A rapid method is proposed for the preparation of binuclear rhodium(II) tetraacetate $[\text{Rh}_2(\text{OAc})_4(\text{HOAc})_2]$ under the action of microwave radiation. This complex is potentially suitable for the coulometric determination of rhodium. The mechanism of the redox process $\text{Rh}_2(\text{III}, \text{II}) \rightleftharpoons \text{Rh}_2(\text{II}, \text{II})$ in acetic acid solutions of this complex has been characterized by cyclic voltammetry, controlled-potential coulometry, and spectrophotometry.

The appropriate selection of an initial compound (depolarizer) and a simple method for its preparation in solution are necessary for the successful development of procedures for the coulometric determination of an element. This is particularly important in the case of rhodium because coulometry is used more rarely for this element than for other platinum-group metals [1].

The data reported in the literature [2–6] indicates that binuclear rhodium(II) tetraacetate $[\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2]$, which is converted to mixed-valence $\text{Rh}_2(\text{III}, \text{II})$ acetate under the action of strong oxidants [6], can serve as a promising depolarizer for the coulometric determination of rhodium. The redox reaction $\text{Rh}_2(\text{III}, \text{II}) \rightleftharpoons \text{Rh}_2(\text{II}, \text{II})$ occurs in solutions of this complex on a Pt electrode in the potential range 1.2–0.5 V. The formal redox potential (E^0) of this process determined by cyclic voltammetry in 1 M H_2SO_4 and 3 M HClO_4 is 1.22 V [3–5]. As determined by coulometry, the number of electrons involved in the redox process is close to one [4].

Binuclear rhodium(II) tetraacetate $[\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2]$ was first obtained by Chernyaev *et al.* [7] on heating a mixture of H_3RhCl_6 with CH_3COOH and $\text{C}_2\text{H}_5\text{OH}$. Further, the preparation procedure was improved [8]. X-ray diffraction analysis revealed that this compound is a dimer in which rhodium atoms are bonded to each other and each of four acetate groups is bonded to two rhodium atoms forming five-membered rings [9]. Because of the strong trans-effect of the Rh–Rh fragment, axial ligands (water molecules) are readily replaced with other ions or molecules [10], in particular, with solvent molecules.

The available potential range of dimeric rhodium tetraacetate oxidation and reduction on a solid elec-

trode [2–5] and the stability of their solutions with respect to oxidation in air and to hydrolysis in weakly acidic solutions make the $\text{Rh}_2(\text{III}, \text{II})/\text{Rh}_2(\text{II}, \text{II})$ system convenient for the coulometric determination of rhodium. However, procedures for the preparation of binuclear tetraacetate described in the literature (with the aim to obtain the individual complex in the solid state in amounts sufficient for its investigation) are unsuitable for analytical practice: these procedures are time consuming, do not provide the quantitative yield, and are inconsistent with the general method of the analysis of rhodium-containing materials. It was briefly reported in [11] that the reduction reaction of rhodium acetate complexes in 0.1 M H_2SO_4 can be used for the determination of rhodium by controlled-potential coulometry. However, the procedure for the preparation of these complexes and the oxidation and reduction potentials were not presented.

In this work, we used microwave radiation for accelerating and simplifying the preparation of solutions of binuclear rhodium tetraacetate and for increasing its yield. Microwave radiation overcomes the kinetic inertness of compounds and simplifies the replacement of ligands in the initial complex (replacement of Cl^- ions with CH_3COOH molecules in our case). The efficiency of the use of microwave radiation for the synthesis of complex compounds was noted in review [12] and confirmed in several works where this technique was used for the preparation of complexes used in analytical chemistry in combination with spectrophotometry [13, 14], luminescence [15], and coulometry [16].

The aim of this work was to find the optimal conditions of the preparation of binuclear rhodium tetraac-

tate, which is the initial compound for the coulometric determination of rhodium, with microwave heating, to study its electrochemical properties, and to compare them with the properties of rhodium tetraacetate synthesized by the conventional method [8].

EXPERIMENTAL

Initial compounds, apparatus, and procedure.

Initial compounds for the synthesis of binuclear rhodium(II) tetraacetate under the action of microwave radiation were $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$ (34% Rh), glacial CH_3COOH (chemically pure), and 98% ethanol. The concentration of rhodium in studied solutions was $n \times 10^{-4}$ – $n \times 10^{-3}$ M. As model solutions, we used acetic acid solutions prepared from $[\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2]$ (20.69% C, 3.29% H).

Microwave irradiation was performed in an MDS-2000 microwave oven (CEM Corp., USA) in closed LDV autoclaves at $P = 270$ W. The temperature was monitored with an optical fiber probe inserted into the autoclave. The volume of solutions was ~ 10 – 11 mL.

Procedure. A mixture of $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$ (1.5–15 mg), 10 mL of CH_3COOH (5–17.5 M), and 0.1–1.0 mL of $\text{C}_2\text{H}_5\text{OH}$ were placed in an autoclave; the autoclave was mounted in a microwave oven and irradiated for 5–15 min at 100–150°C in the thermostatic mode. After microwave irradiation, solutions were cooled to room temperature, transferred into volumetric flasks, and diluted to the required volume with acetic acid of the selected concentration.

Cyclic voltammograms were recorded in the range 0.00–1.20 V at the potential scanning rate (ν) from 5 to 200 mV/s on a PA-4 polarographic analyzer (Czech Republic). Coulometric measurements were performed using a PI-50-1 potentiostat (Belarus) and an IP-12 current integrator (Vernadsky Institute of Geochemistry and Analytical Chemistry, Russia) of 0.1 accuracy class. A three-chamber electrolyzer was used in both electrochemical methods. A Pt disk ($\varnothing = 0.2$ mm) was used as the indicator electrode in cyclic voltammetry, and a Pt net ($S = 100$ cm²) was used as the working electrode in controlled-potential coulometry. In both methods, a Pt helix was used as the auxiliary electrode and a saturated calomel electrode was used as the reference electrode. As the supporting electrolyte, we used CH_3COOH of the same concentration as in microwave irradiation (5–17.5 M). Bubbling with argon was used for stirring solutions and for removing oxygen from solution. The amount of rhodium was determined by the successive oxidation and reduction of acetate solutions obtained on microwave irradiation at potentials found from the characteristics of cyclic voltammograms.

Electronic absorption spectra were recorded on a Specord UV VIS spectrophotometer (Germany) in the wavelength range from 250 to 800 nm in quartz cells with $l = 1.0$ or 5.0 cm.

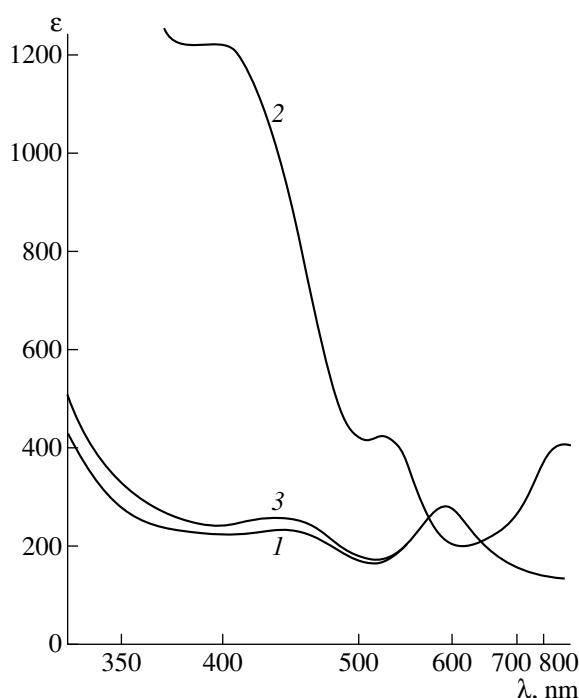


Fig. 1. Electronic absorption spectra of binuclear rhodium tetraacetate obtained on microwave irradiation under optimal conditions; 1×10^{-3} M C_{Rh} , 11.7 M $C_{\text{CH}_3\text{COOH}}$; (1) initial solution, (2) solution 1 after oxidation at $E = 1.10$ V, and (3) solution 2 after reduction at $E = 0.70$ V.

RESULTS AND DISCUSSION

Acetic acid solutions of rhodium complexes obtained on the microwave irradiation of mixtures of rhodium(III) chloride, CH_3COOH , and ethanol are blue. The parameters of the electronic spectra ($\lambda_{\text{sh}} = 440$ – 450 and $\lambda_{\text{max}} = 590$ nm) and cyclic voltammograms ($E_{\text{p,a}} = 0.94$ V, $E_{\text{p,c}} = 0.89$ V) of these solutions coincide with the parameters obtained for solutions of the model complex in CH_3COOH of the corresponding concentration (Fig. 1, curve 1 and Fig. 2, curve 2) and are very close to the parameters assigned in the literature to solutions of $[\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2]$ in H_2SO_4 , NaClO_4 , and other media [2, 3, 6]. Insignificant differences from the latter (about 10 nm in spectra and about 0.10 V in voltammograms) can be explained by the replacement of axial ligand water molecules in complexes with CH_3COOH molecules [17] with the formation of $[\text{Rh}_2(\text{OAc})_4(\text{HOAc})_2]$.

In the selection of conditions of microwave irradiation, the completeness of the conversion of RhCl_3 to the desired complex was estimated from the coulometric results obtained by the reduction reaction $\text{Rh}_2(\text{III}, \text{II}) \rightarrow \text{Rh}_2(\text{II}, \text{II})$. The table presents the optimal conditions of the preparation of binuclear rhodium tetraacetate with microwave irradiation selected as a result of the measurements of several parameters.

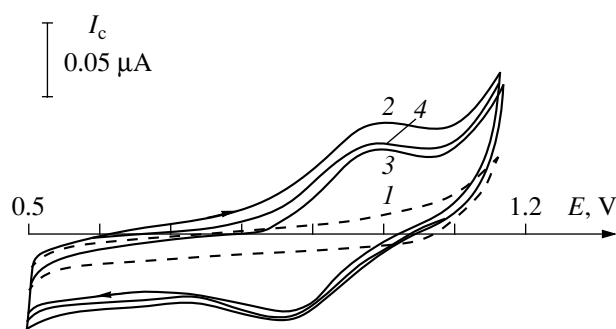


Fig. 2. Cyclic voltammograms of a solution of binuclear rhodium tetraacetate obtained on microwave irradiation under optimal conditions; 1×10^{-3} M c_{Rh} , 11.7 M $c_{\text{CH}_3\text{COOH}}$, $v = 50$ mV/s, Pt electrode; (1) supporting solution, (2) initial solution, (3) solution 2 after oxidation at $E = 1.10$ V, and (4) solution 3 after reduction at $E = 0.70$ V.

An increase in the concentrations of CH_3COOH and $\text{C}_2\text{H}_5\text{OH}$ up to the optimal values (see table) increases the yield of the desired complex. A further increase in the concentrations of these components of the mixture leaves the yield unchanged. As the temperature increases from 110 to 140°C , the yield of rhodium acetate gradually increases, and at higher temperatures gradually decreases, possibly, because of the decomposition of the complex. The same effect is observed upon an increase in the heating time above 10 min. The precipitation of rhodium tetraacetate is not observed in microwave irradiation, whereas it occurs in conventional heating [7, 8]. The time consumed for the preparation of dimeric rhodium acetate with microwave irradiation is smaller by an order of magnitude than that with conventional heating. Under the optimal conditions, the yield is close to 100%, whereas for conventional heating it is no higher than 75%.

The spectrum of the solution obtained at the concentration of CH_3COOH below 8.8 M exhibits an additional band with $\lambda_{\text{max}} = 350$ nm ($\epsilon = 290$) along with the main bands with $\lambda_{\text{max}} = 440$ and 590 nm. Possibly, this

Selection of optimal conditions of the preparation of $[\text{Rh}_2(\text{OAc})_4(\text{HOAc})_2]$ with microwave irradiation ($P = 270$ W)

Parameter	Variation range of the parameter	Optimal conditions
$c_{\text{CH}_3\text{COOH}}$, M (volume ratio $\text{CH}_3\text{COOH} : \text{H}_2\text{O}$ from 1 : 0 to 3 : 1)	5–17.5	11.7
$c_{\text{C}_2\text{H}_5\text{OH}}$, M	0–1.55	1.55
Temperature, $^\circ\text{C}$	110–150	140
Time, min	5–15	10
$c_{\text{RhCl}_3 \cdot 4\text{H}_2\text{O}}$, mg/mL	0.05–0.23	>0.10

is due to the formation of a by-product, e.g., triacetate $[\text{Rh}_2(\text{OAc})_3]^+$, whose spectrum exhibits a shoulder at 357 nm [3]. The presence of this complex in the solution has no effect on cyclic voltammograms because its oxidation and reduction potentials are close to the corresponding potentials of tetraacetate [2]. Upon increasing the concentration of CH_3COOH , the band at 350 nm disappears. In some experiments, the intensity of the absorption bands at 440 and 590 nm in solutions after microwave irradiation was lower than in solutions of the model complex by 13–15%, possibly, because of the formation of some amount of the oxidized (mixed-valence) $\text{Rh}_2(\text{III}, \text{II})$ complex. The presence of the oxidized form has no effect on the results of coulometric determination. Note that after both microwave irradiation and conventional heating, ethyl acetate is formed in solutions as a result of the interaction between excess CH_3COOH and $\text{C}_2\text{H}_5\text{OH}$.

The electrooxidation of a blue solution of $[\text{Rh}_2(\text{OAc})_4(\text{HOAc})_2]$ prepared by microwave irradiation at $E_0 = 1.10$ V yields an orange–yellow solution of the $[\text{Rh}_2(\text{OAc})_4(\text{HOAc})_2]^+$ complex, whose spectrum exhibits absorption bands with λ_{max} 400 (1338), 510 (420), and 780 (450) nm (Fig. 1, curve 2). These bands are very close in characteristics to those for a solution of the model salt oxidized under the same conditions and close to the data reported in the literature for solutions of this complex in H_2SO_4 . The comparison of the absorption spectra of freshly prepared and aged solutions of the initial $\text{Rh}_2(\text{II}, \text{II})$ complex and the oxidized $\text{Rh}_2(\text{III}, \text{II})$ complex demonstrated that the initial complex is stable in time, whereas the $\text{Rh}_2(\text{III}, \text{II})$ complex is gradually reduced within two days converting into the initial $\text{Rh}_2(\text{II}, \text{II})$ complex. A similar process was observed previously in oxidized solutions of binuclear rhodium(III, II) tetrasulfates [18]. Oxidized $\text{Rh}_2(\text{III}, \text{II})$ tetraacetate is converted to the initial $\text{Rh}_2(\text{II}, \text{II})$ complex on electroreduction at $E_r = 0.60$ – 0.70 V. This fact is confirmed by the nearly full coincidence of the spectra and voltammograms of the initial and reduced solutions (Fig. 1, curves 1, 3 and Fig. 2, curves 1, 3) and indicates that the complex retains its dimeric Rh–Rh core on oxidation and reduction.

The redox system of $\text{Rh}_2(\text{III}, \text{II})/\text{Rh}_2(\text{II}, \text{II})$ acetate complexes was studied in detail by cyclic voltammetry to find out if it can be used for the coulometric determination of rhodium. Cyclic voltammograms characterizing this system in 17.5 M CH_3COOH as the supporting electrolyte exhibit two peaks at $E_{\text{p,a}} = 0.95$ V and $E_{\text{p,c}} = 0.89$ V at v from 10 to 200 mV/s. The formal redox potential (E^0) of the studied system in 17.5 M CH_3COOH was determined from the value of E at I_p corresponding to 85% of the maximum height of oxidation (or reduction) current peaks [19] (1.18 ± 0.02 V relative to the H electrode). This value of E^0 is very

close to the E^0 determined by the authors of [3–5] in 0.1 M H_2SO_4 and 3 M $HClO_4$.

At $v = 10\text{--}100$ mV/s, the values of $E_{p,a}$ and $E_{p,c}$ are nearly independent of v , and $I_{p,a}$ and $I_{p,c}$ linearly increase with v and $v^{1/2}$, respectively, which is indicative of the reversibility of the process. The slope of the dependence of $\log I_p$ on $\log v$ (Semerano coefficient) is 0.53 for both anode and cathode current peaks, which is indicative of the diffusion character of the process. The value of ΔE for the anode and cathode current peaks at $v = 10\text{--}200$ mV/s is 40–60 mV, and the ratio $I_a : I_c = 1.06\text{--}1.08$, which is characteristic of a one-electron reversible process. However, at $v < 10$ mV/s, $I_{p,a}$ is larger than $I_{p,c}$, which is characteristic of cases when an electrochemical chemical process is accompanied by a chemical process. The presence of a process accompanying electron transfer at low potential scanning rates is also supported by the \surd -shaped dependence of $I_p v^{1/2}$ on v with an inflection at $v = 20$ mV/s [20].

Thus, diagnostic criteria [19, 20] demonstrated that the one-electron electrode process in acetic acid solutions of binuclear rhodium tetraacetate obtained under the action of microwave radiation is diffusion-controlled and reversible at $v > 15\text{--}20$ mV/s, and at slower potential scanning, electron transfer is accompanied by a chemical process. The redox process $Rh_2(III, II)/Rh_2(II, II)$ in acetic acid solutions of the model complex is of the same character. The presence of the chemical stage along with the electrochemical stage must be taken into account in coulometric experiments, which require much more time than a recording of cyclic voltammograms. We obtained satisfactory results in preliminary experiments on the coulometric determination of 0.2–2.0 mg of rhodium; the procedure included the oxidation of acetate solutions obtained on microwave irradiation at $E = 1.10$ V and subsequent reduction of the oxidized product at $E = 0.70$ V.

Thus, in this work we demonstrated that microwave irradiation can be combined with the coulometric determination of rhodium based on the redox reaction in acetic acid solutions of binuclear rhodium(II) tetraacetate.

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