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ARTICLES

Effect of Microwave Radiation on the Complexation of Rhodium(III) and Iridium(IV) with Reagents of the Pyridylazoresorcinol Group

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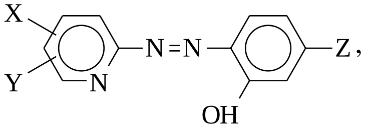
Abstract—It is demonstrated that microwave radiation can be used for the development of simple and rapid procedures for the determination of rhodium and iridium.

Microwave radiation finds increasing application in analytical chemistry. It significantly accelerates the preparation of metallurgical, geological, environmental, etc. samples. Microwave radiation can be efficiently used in the decomposition of biological materials and the sample preparation of organic compounds for analysis in pharmaceutical and other industries. There are publications dealing with the peculiarities of the reactions of hydrolysis, oxidation, complexation, etc. under the action of microwave radiation [1–3]. However, these processes, complexation in particular are still insufficiently studied. Partly this is due to analytical laboratories with devices for microwave treatment providing control of the time of the process, radiation power, and temperature and pressure in a hermetically sealed autoclave. Nevertheless, even the use of home microwave ovens makes it possible to study conditions of complexation at different heating modes and to draw reliable conclusions. Commonly, complexation processes under the action of microwave radiation and without it significantly differ in the time and completeness of reactions. In many cases, this provides substantial gain in the time and completeness of reactions.

With the aim to develop a procedure for the determination of rhodium and iridium, in this work we studied the interaction of these elements with reagents of the 4-(2-pyridylazo)resorcinol (PAR) group and their bromine derivatives: 1-(2-pyridylazo)-5-aminophenol (PAAP), 1-(3,5-dibromo-2-pyridylazo)-5-aminophenol (3,5-di-Br-PAAP), and 1-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol (3,5-di-Br-PADAP)



where X, Y, and Z are –H, –Br, $–NH_2$, and $–N(C_2H_5)_2$. For all three reagents, we studied complexation under the action of microwave radiation of different powers and without microwave radiation; a high sensitivity of color reactions was demonstrated.

EXPERIMENTAL

We used 4×10^{-4} M solutions of rhodium(III) and iridium(IV). A stock solution of iridium(IV) (1×10^{-3} M) was prepared by dissolving a weighed portion of potassium hexachloroiridate in 1 M HCl. The concentration of iridium in the solution was verified spectrophotometrically by the reaction with *o*-dianisidine [4]. A stock solution of rhodium(III) was prepared by dissolving a weighed portion of $RhCl_3 \cdot 6H_2O$ in concentrated HCl and subsequent evaporation to wet salts. The residue was dissolved in 6 M HCl. The concentration of rhodium in the solution was determined spectrophotometrically using tin(II) chloride [5, 6]. Working solutions of rhodium(III) and iridium(IV) were prepared by the dilution of stock solutions with 1 M HCl.

Solutions of reagents (1×10^{-3} and 4×10^{-4} M) were prepared by dissolving weighed portions in isopropanol and stored in dark glass bottles. The constancy of reagent concentration was checked spectrophotometrically. The absence of organic impurities was checked by thin-layer chromatography on Silufol plates.

Ascorbic, formic, lactic, acetic, and oxalic acids and isopropanol of analytical grade were used without additional purification.

The required pH was adjusted with an acetate–isopropanol buffer mixture, which was prepared as follows. Twenty-five milliliters of a 0.2 M CH_3COONa solution, 3.5 mL of 1 M CH_3COOH, 50 mL of isopropanol, and 170 mL of water were placed in a 250-mL volumetric flask. The buffer mixture was either stored for 2 h in a boiling water bath or exposed to microwave radiation in a microwave oven for 5 min in the “high” mode. The solutions were cooled to room temperature and the pH was checked. If necessary, the pH was

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adjusted to the required value (4.2 ± 0.4 for rhodium and 5.2 ± 0.4 for iridium, see below) by the addition of a 0.2 M NaOH solution or 1 M CH_3COOH, and the solutions were diluted with distilled water to the mark. When microwave radiation was used, the buffer mixture was heated in a 1-L beaker and transferred into a volumetric flask after cooling. Buffer mixtures can be used for two weeks on storage at room temperature.

The pH value was checked with pH-121 and pH-150 millivoltmeters. Absorption spectra of solutions were recorded on Specord UV-Vis and KFK-3 spectrophotometers in cells with the thickness of the absorbing layer being 2 and 5 cm, respectively. For microwave irradiation, we used a Goldstar-MA-892TD home microwave oven with a frequency of 2450 MHz in the modes “low,” “med,” “med-high,” and “high,” which correspond to 20–100% of the rated power of 900 W.

RESULTS AND DISCUSSION

The experimentally determined optimal pH for the complexation reactions of rhodium(III) and iridium(IV) with reagents of the PAR group are 4.2 ± 0.4 for rhodium and 5.2 ± 0.4 for iridium. As buffer mixtures for adjusting the optimal pH in the system, we studied acetate, phosphate, and universal mixtures [7] prepared with the addition of isopropanol. In all cases, we compared the results obtained by the exposure of buffer systems to microwave radiation or prolonged heating or merely by mixing the components of buffer systems. All three buffer systems yielded comparable results; however, the isopropanol–acetate mixture is the simplest in preparation and yields most stable results.

In all of the studied buffer systems prepared without heating or microwave irradiation, the sensitivity of reactions is lower by 30–60%.

It was demonstrated that the absorbance gradually increases on heating buffer mixtures for 1 and 1.5 h and remains constant after heating for 2 h. When buffer mixtures were exposed to microwave radiation in the “high” mode, the above effect was attained within 5 min.

To reveal the mechanism of the activation of rhodium and iridium, we studied the complexation of these elements with the reagents in the presence of lactic, formic, oxalic, ascorbic, and acetic acids. In this case, instead of the acetate–isopropanol buffer mixture, we used a 20% aqueous solution of isopropanol to which 1 mL of a 0.1 M solution of the acid under study was added per 25 mL of the reaction mixture. The pH of the solution was checked with a pH meter and adjusted to the optimal values by the addition of a 0.2 M NaOH solution. After heating or exposure to microwave radiation, the solutions were diluted to the mark with a 20% aqueous solution of isopropanol.

It was demonstrated that, when lactic, formic, ascorbic, and acetic acids are used in optimal amounts (1 mL of a 0.1 M solution per 25 mL of the reaction mixture), the spectra of the resulting complexes are nearly identical. When these acids are added in amounts larger than optimal, metal complexes are decomposed, probably, because of redox processes. In the presence of oxalic acid, complexes are not formed. Reactions at optimal pH adjusted by the addition of HCl to the water–isopropanol system also do not lead to the formation of complexes.

The addition of the above acids except oxalic in optimal amounts to the reaction mixture with the use of the acetate–isopropanol buffer system does not lead to noticeable changes in the complexation reaction.

We assume that the activation of rhodium(III) and iridium(IV) in complexation reactions with reagents of

Characteristics of color reactions of rhodium and iridium with studied reagents; optimal pH: 4.2 ± 0.4 for Rh and 5.2 ± 0.4 for Ir ($n = 3$; $p = 0.95$)

Element	Reagent	Ratio Me : R	λ_{max}, nm reagent	λ_{max}, nm complex	$\Delta\lambda$, nm	$\varepsilon \times 10^{-4}$
Rh	PAAP	1 : 1	430	500	70	1.6 ± 0.3
		1 : 2	430	510	80	0.6 ± 0.2
	3,5-di-Br-PAAP	1 : 1	440	540	100	1.6 ± 0.2
		1 : 2	440	540	100	–
	3,5-di-Br-PADAP	1 : 1	450	590	140	2.1 ± 0.3
		1 : 2	450	590	140	–
Ir	PAAP	1 : 1	430	530	100	1.6 ± 0.3
		1 : 2	430	530	100	0.8 ± 0.2
	3,5-di-Br-PAAP	1 : 1	440	560	120	–
		1 : 2	440	560	120	–
	3,5-di-Br-PADAP	1 : 1	450	580	130	2.3 ± 0.3
		1 : 2	450	580	130	–

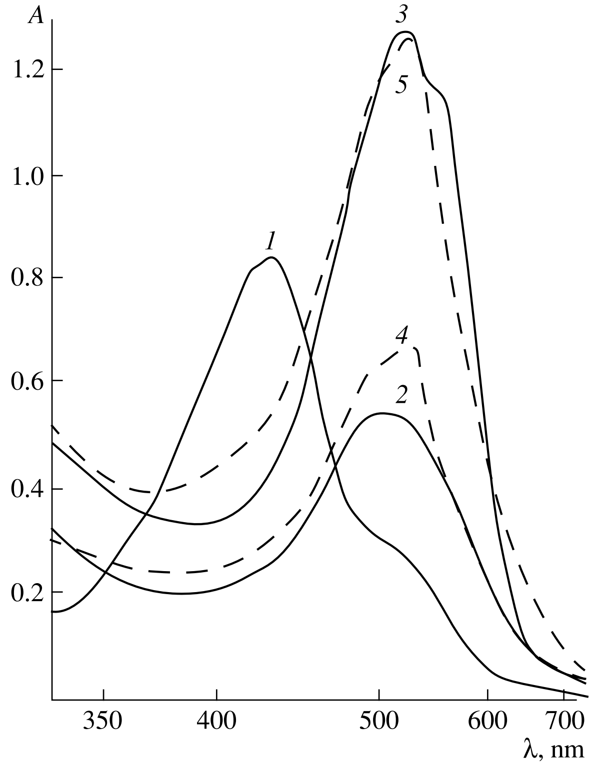

Fig. 1. Absorption spectra of solutions of (*1*) PAAP; (*2*) 1 : 1 and (*3*) 1 : 2 complexes of rhodium; and (*4*) 1 : 1 and (*5*) 1 : 2 complexes of iridium with reference to water (l = 5 cm).

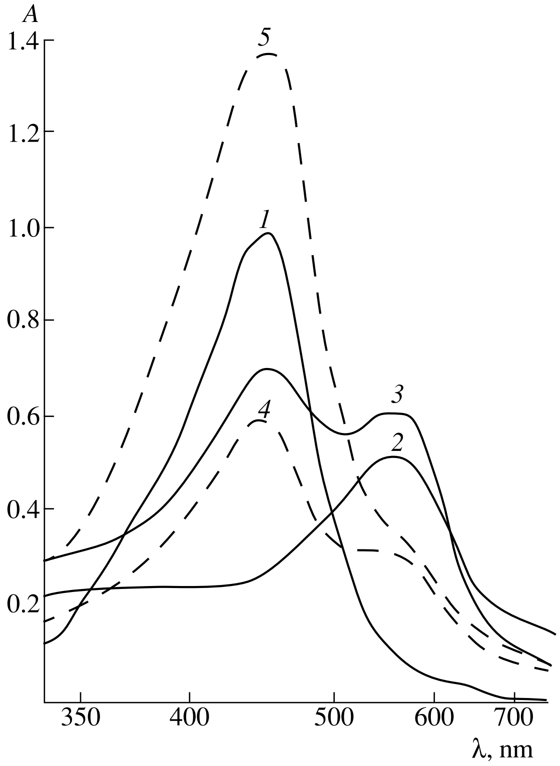

Fig. 2. Absorption spectra of solutions of (*1*) 3,5-di-Br-PAAP; (*2*) 1 : 1 and (*3*) 1 : 2 complexes of rhodium; and (*4*) 1 : 1 and (*5*) 1 : 2 complexes of iridium with reference to water (l = 2 cm).

the PAR group necessarily requires the stage of formation of esters of organic acids and isopropanol and the subsequent formation of rhodium and iridium carbonyl chlorides, which enter into reactions with these reagents [6, 8]. To reveal the role of esters, we studied the formation of rhodium(III) complexes in the presence of ethyl acetate and diisopropyl ether. For this purpose, 4 mL of ethyl acetate or diisopropyl ether was added to 20 mL of an aqueous solution containing the necessary amounts of rhodium and the reagent at optimal pH; next, solutions were heated on a boiling bath for 3 h or exposed to microwave radiation in the “low” mode for 6 min. In all cases, the reagent was nearly immediately and completely extracted with the ester or ether, and the complexation reaction occurred clearly at the phase boundary. Diisopropyl ether is less volatile; therefore, the effect of the reaction was more clear. It was rather difficult to obtain quantitative characteristics of the reaction under these conditions. However, the addition of 20% isopropanol to the two-phase system after the end of the reaction leads to the dissolution of all components of the mixture, and the spectra of the resulting solutions are identical to the spectra obtained by conventional procedures.

Complex compounds were obtained as follows. Portions of a 4×10^{-4} M hydrochloric solution of rhodium(III) or iridium(IV) (1 mL) were placed in 25-mL volumetric flasks, 15–18 mL of a buffer mixture and

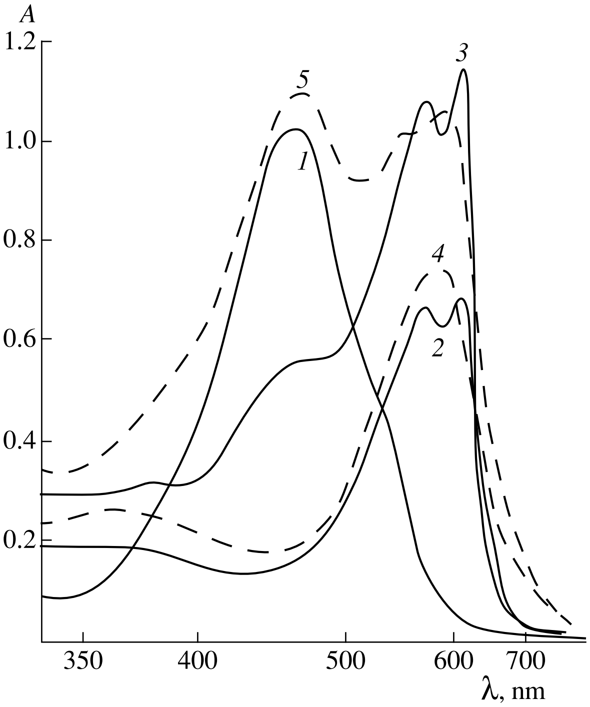

Fig. 3. Absorption spectra of solutions of (*1*) 3,5-di-Br-PADAP; (*2*) 1 : 1 and (*3*) 1 : 2 complexes of rhodium; and (*4*) 1 : 1 and (*5*) 1 : 2 complexes of iridium with reference to water (l = 2 cm).

1 or 2 mL of a 4 × 10^{-4} M isopropanol solution of the reagent were added, and the solutions were kept for 2 h on a boiling water bath or exposed to microwave radiation in the “med-high” mode for 3 min for rhodium and 15 min for iridium (in all cases, the temperature of the reaction mixture was 95–98°C). After the end of the reaction, the solutions were cooled to room temperature and diluted to the mark, and the absorbance of solutions was measured with reference to water (l = 2 or 5 cm). The spectrophotometric characteristics of rhodium and iridium complexes (table) were obtained on heating or exposure to microwave radiation.

The ratio of components in complexes was determined by the isomolar series and saturation methods.

Figures 1–3 present the absorption spectra of rhodium and iridium complexes in an acetate–isopropanol buffer mixture obtained on the irradiation of solutions in a microwave oven.

In the absence of a hermetically sealed autoclave, we failed to provide complete conversion of iridium into 1 : 2 complexes with all studied reagents because of a significant evaporation of the reaction mixture. However, the yield of reaction products can be increased using repeated fractional treatment with microwave radiation. We expect that when the reaction is conducted in a hermetically sealed autoclave under the action of microwave radiation, all difficulties mentioned above can be resolved and the sensitivity of the reaction will be significantly increased.

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