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Thiopyrazolone Derivatives as Analytical Reagents. XV.[1] Spectrophotometric Determination of Osmium with Thiopyrine

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A spectrophotometric method for the determination of micro-amount of osmium with thiopyrine was established, based on the formation of water-soluble bluish green complex, which shows an absorption maximum at 740 nm. The absorbance of the complex was constant over the pH range of 0.5—1.8. The addition of 2-propanol was effective to increase and maintain the absorbance. The method was satisfactorily applied to the concentration less than 20 μg/ml. The molar absorptivity was found to be 1.20×10^4 $l \cdot cm^{-1} \cdot mol^{-1}$. Various common foreign ions and other noble metal ions hardly interfered the determination. The isolated complex was confirmed to be hexakis(thiopyrine)-osmium(IV) perchlorate, by elementary analysis and the molar conductivity determined in acetonitrile.

Keywords——osmium(VIII); thiopyrine; spectrophotometry; bluish green complex; absorption maximum at 740 nm; aqueous 2-propanol solution; hexakis(thiopyrine)osmium (IV) perchlorate

In my earlier work,[3] it was reported that thiopyrine (2,3-dimethyl-1-phenyl-3-pyrazoline-5-thione) behaved as a sulfur donor-type monodentate ligand to form water-soluble complexes with a number of metal ions. Almost of the thiopyrine-metal complexes were colorless, but palladium (II), bismuth (III), selenium (IV) and tellurium (IV) gave orange complexes, and ruthenium (III) and osmium (VIII) gave bluish green complexes. The author has already reported on the spectrophotometric determination of selenium,[4a] ruthenium[4b] and palladium[1] with thiopyrine. This reagent has also been applied to the masking of copper, mercury and thallium in chelatometric titrations.[5] In this paper, an application of thiopyrine to the spectrophotometric determination of osmium is described. The proposed method is more simple, selective and sensitive than thiourea method[6] which is commonly used for the determination of osmium.

Experimental

Reagents——The thiopyrine was prepared as previously described,[7] and used as an approximately 1% aqueous solution. A standard osmium(VIII) solution was prepared by dissolving a definite amount of pure osmium tetroxide in distilled water, and it was standardized by thiourea method[6] spectrophotometrically. All other reagents used in the experiment were of reagent grade.

Apparatus——The measurements of absorbance were made with a Shimadzu spectrophotometer QV-50 with 1 cm glass cells. The measurements of pH were made with a Horiba glass electrode pH meter Model M5. The measurements of conductance were made at 25° with a Yanagimoto conductivity meter Model MY-8 with a conventional cell, previously calibrated with an aqueous solution of potassium chloride.

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[4] *a*) T. Tanaka, *Bunseki Kagaku*, **20**, 291 (1971); *b*) *Idem*, *idid.*, **26**, 597 (1977).

[5] T. Tanaka, *Yakugaku Zasshi*, **93**, 252 (1973).

[6] G.H. Ayres and W.N. Wells, *Anal. Chem.*, **22**, 317 (1950); W.J. Allan and F.E. Beamish, *ibid.*, **24**, 1608 (1952); F.E. Beamish, "The Analytical Chemistry of the Noble Metals," 1st ed., Pergamon Press, Inc., Oxford, 1966, p. 400.

[7] T. Tanaka, *Yakugaku Zasshi*, **91**, 311 (1971).

Recommended Procedure for Determination——The sample solution, containing less than 450 μg of osmium(VIII), and 10 ml of 2-propanol were taken into a 25 ml volumetric flask. The pH of the solution was then adjusted to about 0.8—1.5 with 1 M sulfuric acid. To this solution, 2 ml of 1% thiopyrine solution was added, and the mixture was diluted to 25 ml with water. After standing for 5 min, the absorbance of the solution was measured at 740 nm against water.

Preparation of Hexakis(thiopyrine)osmium(IV) Perchlorate——To 30 ml of 0.1 N sulfuric acid solution containing 25 mg of osmium tetroxide was added an excess of thiopyrine solution prepared by dissolving 800 mg of thiopyrine in 20 ml of 2-propanol. The bluish green solution obtained was allowed to stand for 5 min and 30 ml of 5% sodium perchlorate solution was then added with stirring. Blue-colored precipitates formed immediately were filtered off, well washed with 0.1% sodium perchlorate solution and then with water, and dried *in vacuo* over P_2O_5. The yield was 170 mg. mp 178—180° (dec.). *Anal.* Calcd. for $C_{66}H_{72}Cl_4N_{12}O_{16}OsS_6$: C, 43.70; H, 4.00; N, 9.27. Found: C, 43.62; H, 3.98; N, 9.25.

Results and Discussion

Absorption Spectrum

Osmium (VIII) reacted with thiopyrine in a solution acidified with diluted sulfuric or hydrochloric acid to form a bluish green complex. An absorption maximum was observed at 740 nm in the absorption spectrum of the complex, as shown in Fig. 1. Accordingly, all of the absorbance measurements in this study were made at 740 nm.

Effect of pH

The effect of pH was studied on the formation of osmium-thiopyrine complex. Diluted sulfuric or hydrochloric acid and sodium acetate solution were used for the adjustment of pH. The results are shown in Fig. 2. The highest and stable absorbance was obtained in the pH range of 0.5 and 1.8.

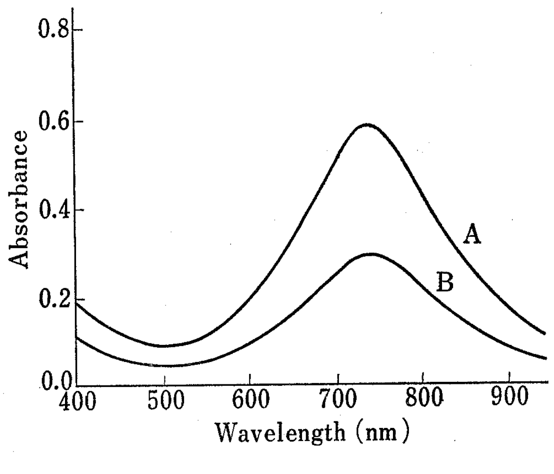

Fig. 1. Absorption Spectra of Osmium-thiopyrine Complex

A: 9.20 μg/ml Os(VIII),
B: 4.60 μg/ml Os(VIII).
Measurements were carried out by the recommended procedure.

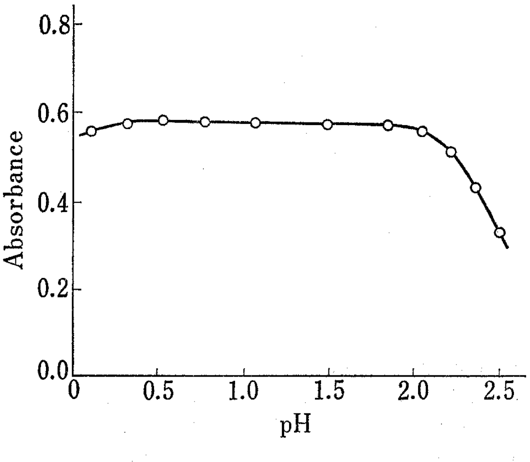

Fig. 2. Effect of pH on the Absorbance

Os(VIII): 9.20 μg/ml, 1% thiopyrine: 2 ml, 2-propanol: 10 ml, total volume: 25 ml, wavelength: 740 nm, reference: water.

Effect of the Amount of Reagent

The effect of the reagent concentration was studied with solutions containing a given amount of osmium and varying amounts of a 1% thiopyrine solution. The results are shown in Fig. 3. When 0.5 ml or more of the reagent solution was added, the absorbance was nearly constant. Accordingly, 2 ml of the reagent solution was used in the recommended procedure.

Effect of the Addition of 2-Propanol

In the reaction of osmium (VIII) with thiopyrine without addition of 2-propanol, the color of solution was unstable and the absorbance at 740 nm rapidly decreased on standing. However in the presence of some organic solvent, such as methanol, ethanol, 2-propanol and

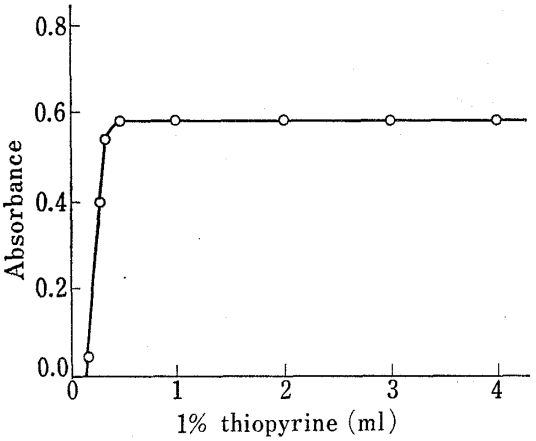

Fig. 3. Effect of Amount of Reagent on the Absorbance

Os(VIII): 9.20 μg/ml, pH: 1.0.
The other conditions are the same as those in Fig. 2.

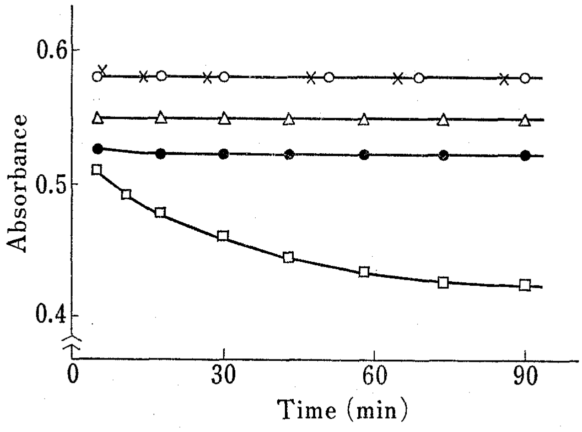

Fig. 4. Effect of Standing Time in Aqueous 2-Propanol Solution of Various Concentration on the Absorbance

Os(VIII): 9.20 μg/ml, pH: 1.0.
2-Propanol: —□—: 0 ml, —●—: 2.5 ml, —△—: 5 ml, —○—: 10 ml, —×—: 15 ml.
The other conditions are the same as those in Fig. 2.

Table I. Effect of Foreign Ions on the Determination of Osmium

Foreign ion	Added as	Amount of ion (μg/ml)	Absorbance at 740 nm
None	—	—	0.580
Zn(II)	$ZnSO_4 \cdot 7H_2O$	240	0.575
Cd(II)	$CdSO_4 \cdot 8/3H_2O$	240	0.575
Pb(II)	$Pb(NO_3)_2$	240	0.570
Hg(II)[a]	$Hg(NO_3)_2 \cdot 1/2H_2O$	200	0.570
Cu(II)	$CuSO_4 \cdot 5H_2O$	30	0.560
Mn(II)	$MnSO_4 \cdot 4H_2O$	220	0.575
Co(II)	$CoSO_4 \cdot 5H_2O$	230	0.575
Ni(II)	$NiSO_4 \cdot 6H_2O$	230	0.580
Cr(III)	$CrK(SO_4)_2 \cdot 12H_2O$	120	0.570
Al(III)	$Al(NH_4)(SO_4)_2 \cdot 12H_2O$	120	0.570
Fe(III)	$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	120	0.575
Bi(III)	$Bi(NO_3)_3 \cdot 5H_2O$	130	0.570
Ag(I)[a]	$AgNO_3$	120	0.570
Pd(II)[a]	$PdCl_2 \cdot 2H_2O$	120	0.570
Rh(III)	$RhCl_3 \cdot 3H_2O$	120	0.580
Au(III)	$HAuCl_4 \cdot 4H_2O$	110	0.565
Ir(IV)	$H_2IrCl_6 \cdot 6H_2O$	130	0.575
Pt(IV)[a]	$H_2PtCl_6 \cdot 6H_2O$	120	0.580
Ru(III)	$RuCl_3 \cdot H_2O$	60	0.600
Sn(IV)[b]	$SnCl_4 \cdot H_2O$	120	0.565
Te(IV)[a]	$K_2TeO_4 \cdot 3H_2O$	120	0.565
V(V)[b]	NH_4VO_3	70	0.600
Mo(VI)[b]	$Na_2MoO_4 \cdot 2H_2O$	120	0.565
W(VI)[b]	$Na_2WO_4 \cdot 2H_2O$	120	0.560
Re(VII)	$KReO_4$	120	0.580

Os(VIII) was taken 9.20 μg/ml.
[a] 4 ml of 1% thiopyrine solution was added to the sample solution.
[b] Metal ions were masked previously by adding 5 ml of 2 M citric acid solution.

acetone, the color was stable and the absorbance fractionally increased. In particular, the addition of 2-propanol was effective. The results are shown in Fig. 4. When 2-propanol was added up to 40% or more to the final volume of the solution, the color development was completed within 5 minutes after the addition of the reagent, and the highest absorbance was maintained at least for an hour. Accordingly, 10 ml of 2-propanol was added in the recommended procedure.

Calibration Curve

A calibration curve which obeys Beer's law over the range of 40—450 μg osmium was obtained by the recommended procedure. The molar extinction coefficient was calculated to be $1.20 \times 10^4\ \mathrm{l \cdot cm^{-1} \cdot mol^{-1}}$. The sensitivity of this method is about three times that of thiourea method.[6]

Effect of Foreign Ions

The effect of foreign ions is shown in Table I. Metal ions such as palladium (II), rhodium (III), bismuth (III), iridium (IV), platinum (IV) and tellurium (IV) which react with thiopyrine to give orange or yellow complexes did not interfere the absorption measurement at 740 nm for the determination of osmium. The interference of ruthenium (III) which forms a bluish green complex[4b] was negligible, although the absorbance of the ruthenium complex at 740 nm was considerably high, because the reaction rate was very low at room temperature in the case of ruthenium. When the large amounts of the metal ions such as silver (I), mercury (II), palladium (II), platinum (IV) and tellurium (IV) were present, the addition of 4 ml of 1% thiopyrine solution was effective to avoid their interferences. The interference caused by the white turbidity, which was produced in the presence of tin (IV), vanadium (V), molybdenum (VI) and tungsten (VI), could be removed by the masking of these metal ions with citric acid.

Composition of the Colored Complex

A blue-colored precipitate formed by the addition of a sodium perchlorate solution in the concentrated reaction solution of osmium (VIII) and thiopyrine in diluted sulfuric acid was confirmed to be hexakis(thiopyrine)osmium (IV) perchlorate, $[\mathrm{Os(C_{11}H_{12}N_2S)_6}](\mathrm{ClO_4})_4$, by elementary analysis. The molar conductance of the 10^{-3} mol/l isolated osmium complex in acetonitrile was determined as $520\ \mathrm{ohm^{-1} \cdot cm^2 \cdot mol^{-1}}$ based on the molecular weight (1813.8), which corresponds to this chemical formula. The validity of this formula was supported by the molar conductance determined, because the value obtained corresponded to that of complex cation with a charge +4, being referred to the values previously obtained with various thiopyrine-metal cationic complexes.[3,4b] The absorption spectrum of the isolated osmium complex at pH 1.0 in 40% 2-propanol aqueous solution was similar to that shown in Fig. 1. The molar extinction coefficient at 740 nm was $1.12 \times 10^4\ \mathrm{l \cdot cm^{-1} \cdot mol^{-1}}$ and the value almost agreed with that obtained from the calibration curve.

It has been well known that octavalent osmium is readily reduced to hexa and tetravalent state and further to lower valency state, while thiopyrine was found to behave as both complexing and reducing agents in the previous studies.[3,8] Being considered these findings, it is reasonable to interpret the reaction presented here, in terms of the reduction and coordination of osmium (VIII) by thiopyrine.

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8) T. Tanaka, *Yakugaku Zasshi*, **91**, 332 (1971).