

ON THE DIOXIMINE COMPLEXES OF TRANSITION METALS. LXXXVII. SPECTROPHOTOMETRIC STUDIES ON THE FORMATION OF SOME RHENIUM COMPLEXES WITH α -SUBSTITUTED ALICYCLIC OXIME DERIVATIVES

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Abstract

The formation conditions, stability in acidic aqueous solutions ($\text{Re(IV)} : \text{oxime} = 1 : 4$) and the analytical application of some rhenium complexes with 1,2-cyclohexane dione dioxime and 1,2-cyclododecanedione dioxime and 1,2,3-cyclohexane trione dioxime (1,3) derivatives: -2-hydrazone, -2-semicarbazone, 2-thiosemicarbazone and -2-phenylhydrazone were studied. The spectrophotometric measurements were carried out in hydrochloric acid medium in the presence of tin(II) chloride as reducing agent.

Introduction

A yellow-brown (reddish-brown) colour reaction occurs in the perrhenate- α -dioxime systems in acidic medium, in the presence of strong reducing agents (SnCl_2 , CrCl_2 , VSO_4 , etc). Some aliphatic- (dimethylglyoxime, glyoxime, methylisopropyl-2,3-dione-dioxime), aromatic- (α -benzyldioxime) and heterocyclic α -dioximes (furyldioxime, pyridyl dioxime) were used for this reaction, especially, from the analytical point of view.

The determination of the composition and stability of these coloured compounds and that of the oxidation state of rhenium in the mentioned derivatives is very difficult owing to the complexity of the system studied (ReO_4 -oxime - reducing agent - mineral acid).

According to some opinions, rhenium is bivalent in these compounds and the formation ration is $\text{Re} : \text{oxime} = 1 : 2$.

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Other authors reported a combination ratio of Re : oxime = 1 : 4 with Re(IV) or Re(V), respectively. FERGUSON et al. assume the formation of Re(dioxime)₃X type derivatives (X = monovalent anion) in analogous conditions. In most cases tin(II) chloride was used as reducing agent. BABKO et al. suppose that Sn takes part in the formation of the coloured rhenium complex. This assumption was not confirmed by isotope exchange studies with ¹¹³Sn. Probably the tin(II) chloride promotes the formation of the rhenium-oxime complexes with Cl-ligands in their composition. In the absence of Cl⁻-ions the absorption of the coloured solutions is shifted towards the ultraviolet region. Chromatographic studies by LAZAREV et al. on the ReO₄⁻-dimethylglyoxime-SnCl₂ system, using strong cation-exchange resins (R-SO₃H) showed that the complex formed had a cationic character.

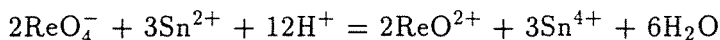
In this paper the formation conditions, stability and analytical applicability of some rhenium-oxime complexes with various α-substituted alicyclic oximes have been studied spectrophotometrically.

Results and Discussion

The electronic spectra of a series of ReO₄⁻ - SnCl₂ - HCl - oxime systems in aqueous solutions were recorded. The following oximes were used: cyclopentanone monoxime, cyclohexanone monoxime, 1,2-cyclohexane dione dioxime, 1,2-cyclododecanedione dioxime, 1,2,3-cyclohexane trione dioxime (1,3) hydrazone (2), ..semicarbazone (2), ..thiosemicarbazone (2), ..phenylhydrazone (2). The electronical spectra are presented in *Fig. 1* and *Fig. 2*.

(The spectra of the phenylhydrazone (2) and cyclododecanedione- dioxime were recorded in 40–60% ethanol).

We observed that the yellow to reddish-brown colour of the solutions appeared on standing for 10–15 minutes and reached its highest intensity after 40–50 minutes. The colour intensity of the 1,2-dione dioxime derivatives does not decrease even on standing for 24 hours. The rhenium complexes with 1,2,3-cyclohexane trione dioxime (1,3)-derivatives are less stable. The slow formation of the complexes is due to the reduction of ReO₄⁻ to Re⁴⁺:



The colour intensity depends on the concentration of HCl and in more concentrated acids, changes also with the time. (See *Figs. 3, 4*).

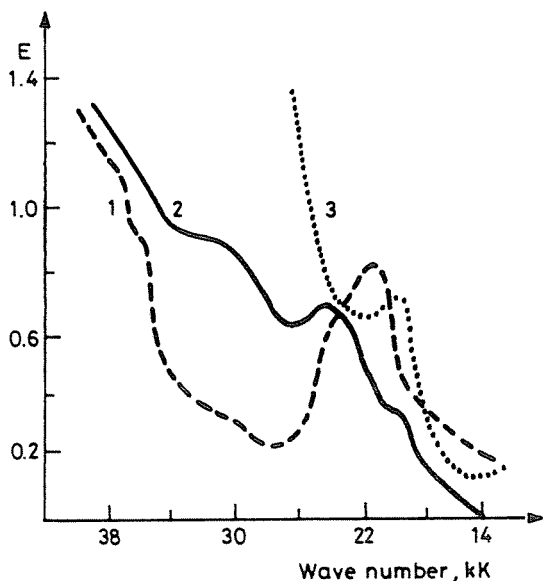


Fig. 1. Electronic spectra of I. Re(IV) - 1,2-Cyclohexane dione dioxime complex, II. Re(IV) - 1,2-Cyclododecanedione dioxime complex, III. Re(IV) - 1,2,3-Cyclohexane trione dioxime (1,3) - hydrazone (2) complex

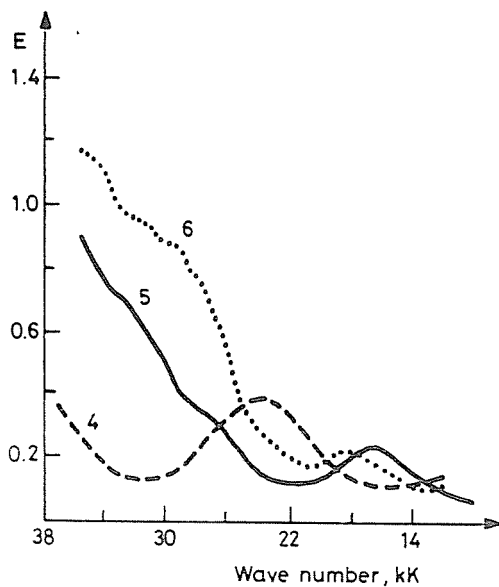


Fig. 2. Electronic spectra of IV. Re(IV) - 1,2,3-Cyclohexane trione dioxime (1,3) - phenylhydrazone (2) complex, V. Re(IV) - 1,2,3-Cyclohexane trione dioxime (1,3) - semicarbazone (2) complex, VI. Re(IV) - 1,2,3-Cyclohexane trione dioxime (1,3) - thiosemicarbazone (2) complex

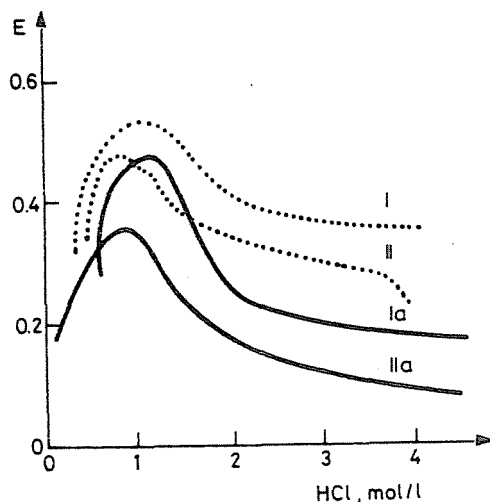


Fig. 3. Influence of the HCl concentration on the optical density of the Re(IV)-oxime solutions. I. Oxime: 1,2-Cyclododecanedione dioxime I after 30 minutes, I* after 24 hours. II. Oxime: 1,2,3-Cyclohexane trione dioxime (1,3) hydrazone (2) II after 30 minutes, II* after 24 hours

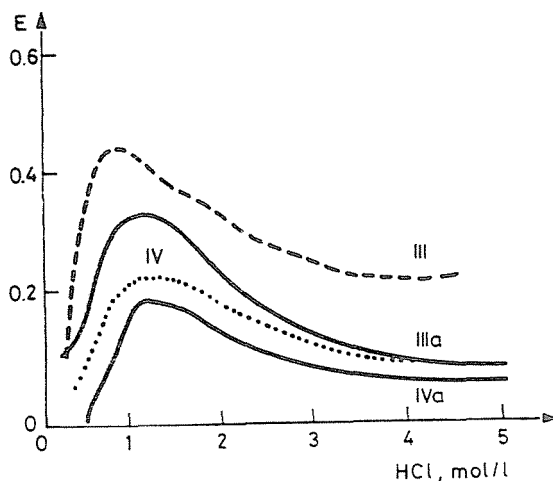


Fig. 4. Influence of the HCl concentration on the optical density of the Re(IV)-oxime solutions. III. Oxime: 1,2,3-Cyclohexane trione dioxime (1,3) semicarbazone (2) III after 30 minutes, III* after 24 hours. IV. Oxime: 1,2,3-Cyclohexane trione dioxime (1,3) thiosemicarbazone (2) IV after 30 minutes, IV* after 24 hours

As shown, the most favourable acidity for the colour formation is 0.5–1 mol/l HCl in the case of the α -dioximes and 0.3–0.6 mol/l HCl for the 1,2,3-trione-dioximes (1,3).

At higher HCl concentrations the bleaching of the solutions can be observed due to the hydrolysis of the chelating agents in strongly acid media.

The spectral data of the complexes are presented in *Table 1*.

Table 1
Electronic spectral data for rhenium(IV)-oxime complexes

Oxime	Band I wave number kK	Molar absorb- tivity	Band II wave number kK	Molar absorb- tivity
1,2-Cyclohexane dione dioxime	22.0	11 700	30 _{inf}	3 900
1,2-Cyclododecane- dione dioxime	23.0	10 000	28–29 _{inf}	9 000
Cyclopentane-one oxime	—	—	—	—
Cyclododecanone oxime	—	—	—	—
1,2,3-Cyclohexane trione dioxime(1,3)-hydrazone (2)	21.0	12 000	28–30	15 000
1,2,3-Cyclohexane trione dioxime(1,3)-semicarbazone (2)	20.5–22.0	5 000	28–30 _{inf}	6 000
1,2,3-Cyclohexane trione dioxime(1,3)-thiosemicarbazone (2)	23–24.0	5 000	28–29 _{inf}	8 000
1,2,3-Cyclohexane trione dioxime(1,3)-phenylhydrazone (2)	24–25.0	9 000	—	—

As shown, the coloured derivatives have two absorption bands in the visible region with maximum at 21–23 kK (band A) and at 28–30 kK (band B), respectively. The molar absorptivity of band A has a value of 10–20 000, and that of band B: 4–5 000. The monoximes do not produce this colour reaction.

On the Composition of the Rhenium-oximine Complexes

The composition of the complexes was determined by Job's method. The isomolar curves of the ReO_4^- -oxime mixtures in the presence of an excess of SnCl_2 in 0.5 mol/l HCl are presented in *Figs. 5–7*.

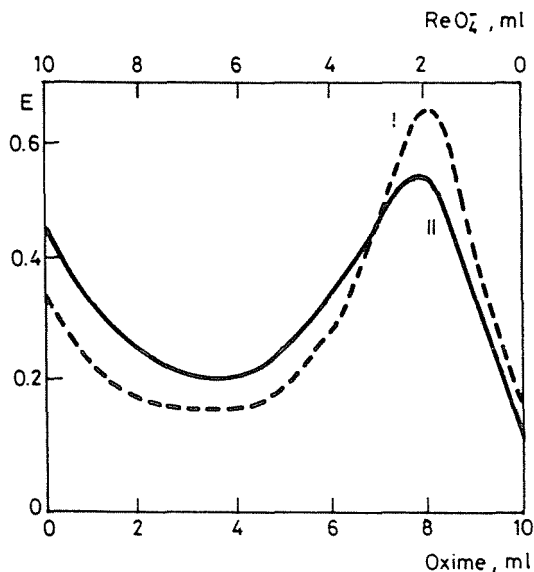


Fig. 5. Job's curves. I. Re(IV)-1,2-Cyclohexane dione dioxime system. II. Re(IV)-1,2-Cyclododecanedione dioxime system

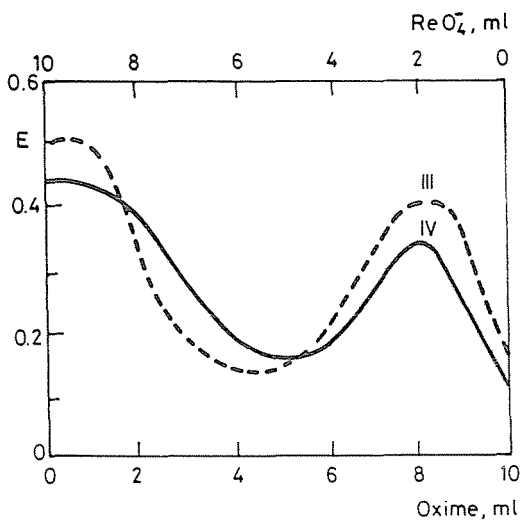


Fig. 6. Job's curves. III. Re(IV)-1,2,3-Cyclohexane trione dioxime (1,2)-hydrazone system. IV. Re(IV)-1,2,3-Cyclohexane trione dioxime (1,2)-phenylhydrazone system

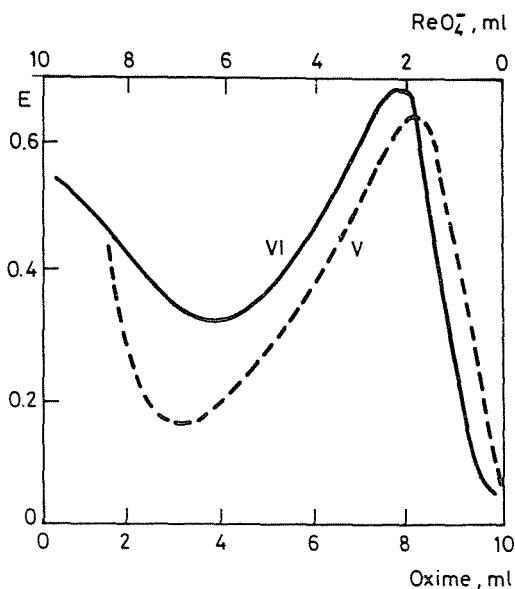


Fig. 7. Job's curves. V. Re(IV)-1,2-Cyclohexane trione dioxime (1,3)-semicarbazone (2) system. VI. Re(IV)-1,2,3-Cyclohexane trione dioxime (1,3)- thiosemicarbazone system

These curves show some deviations from the classical Job's curves which represent the absorption of coloured complexes from colourless components.

At higher $\text{ReO}_4^-/\text{oxime}$ ratios ($>3.5-4$) the green- yellow ReCl_6^{2-} formed first by the reduction with SnCl_2 , has also absorbance. On lowering this ratio the optical density of the mixtures diminishes without having maxima at 1 : 1 and 1 : 2 ratios, respectively. Generally a well-defined maximum appears at a molar ratio $\text{ReO}_4^- : \text{oxime} = 1 : 4$. Thus in contrast with the classical chelates of the α -dioximes with bi- and trivalent transition metals (Fe, Ni, Pd, Pt, Cu, Co, Ir, Rh), with a metal to oxime ratio of 1 : 2, stabilized by two short intramolecular O-H...O hydrogen bridges, in the case of the Re-oxime systems, probably, only classical complexes with a Re to oxime molar ratio of 1 : 4 are formed (e. g. $[\text{Re}(\text{oxime})_4]^{4+}$ or $[\text{ReO}(\text{oxime})_4]^{2+}$, etc.)

It is worth mentioning that in strongly acid medium the oxime molecules appear in the neutral $\begin{matrix} \text{R} \\ \text{R} \end{matrix}$, $\text{C}=\text{NOH}$ or in the monoprotonated form $\begin{matrix} \text{R} \\ \text{R} \end{matrix}$, $\text{C}=\text{NOH}\cdot\text{H}^+$.

Observation: From the alicyclic oximes used the 1,2-cyclohexane dione dioxime, being a colourless, water-soluble reagent, has some advantages. The 1,2-cyclododecanedione dioxime with a large hydrocarbon cycle is soluble only in concentrated alcoholic solutions and by dilution with water a white suspension appears.

Influence of the Nature of the Reducing Agents

Some metal salts in a lower oxidation state (e. g. Cr^{2+} , Ti^{3+} , V^{2+} , etc.) also form coloured Re-oxime complexes in hydrochloric acid medium. The absorbivity of the samples is weaker than in the case of SnCl_2 . In the presence of other nonmetallic reducing agents, e. g. SO_2 , hypophosphite, hydroxylamine, hydrazine, etc. the solutions of rhenium salts remain colourless.

Analytical Applications

The $\text{ReO}_4^- - \text{SnCl}_2 - \text{HCl} - \text{oxime}$ systems follow Beer's law (in a great excess of oxime) in a concentration range of $0.1 \cdot 10^{-5} - 10^{-4}$ mol/l ReO_4^- . At higher rhenium concentrations positive deviations from the straight lines can be observed.

Spectrophotometric determination: $10^{-5} - 2 \cdot 10^{-4}$ mol/l ReO_4^- in 10 ml solution were treated with 2 ml 10% SnCl_2 in HCl (1 : 1) and with 5 ml reagent solution (10^{-2} mol/l) and filled up to 25 ml with 1 mol/l HCl . The optical density of the solutions was measured after standing for an hour, using a green filter. The determination of rhenium with the above mentioned alicyclic oximes is not interfered by most anions, except NCS^- , which forms a red-violet complex under analogous experimental conditions.

Of the transition metal ions a great excess of Cu, Fe, Co (100–1000 fold) interfere with the Re-test having a considerable absorption at about 28–35 kK.

Experimental

1,2-cyclohexane dione dioxime and 1,2-cyclododecanedione dioxime were obtained from the corresponding monoketones by selective oxidation with selenium dioxide, followed by the oximation of the distilled α -diketones with an excess of hydroxylamine hydrochloride in the presence of sodium acetate. The crude products were recrystallized from hot alcohol.

The 1,2,3-cyclohexane trione-dioxime (1,3) derivatives were obtained by the isonitrozation of cyclohexanone with ethyl nitrite in the presence

of acetic acid. The yellow crystalline product was recrystallized from hot alcohol. M.p. of the 2-ketone-1,3-dioximes: 224°C.

This starting material was condensed with stoichiometric amount of semicarbazide, thiosemicarbazide, hydrazine and phenylhydrazine by warming 1–2 hours on a water bath in aqueous-alcoholic solution.

1,2,3-cyclohexane trione dioxime (1,3)-semicarbazone (2) (from water).... m.p. 211–212°C; thiosemicarbazone (2): (from butanol) ... m.p. 173–174°C; ...-hydrazone (2): (from water) ... m.p. 185°C; ... - phenylhydrazone (2): (from methanol): ... m.p. 212°C.

0.01 mol/l oxime solutions were prepared by dissolving 10 mmole of the corresponding chelating agent in 1000 ml water (in some cases in alcohol).

The tin(II) chloride solution was prepared by dissolving 10 g SnCl₂ · 2H₂O (p.a.) in 100 ml 6 mol/l HCl.

The electronic spectra were taken in a strong HCl solution (KReO₄: 2 · 10⁻⁴–6 · 10⁻⁵ mol/l; ReO₄⁻: oxime = 1 : 5) + oxime in excess + 2 ml 10% SnCl₂ + 5 ml 2 mol/l HCl, filled up to 25 ml with water, using a SPECORD spectrophotometer (Carl Zeiss Jena).

The isomolar solutions were prepared from 5 · 10⁻³ mol/l KReO₄ and 5 · 10⁻³ mol/l oxime solutions + 2 ml SnCl₂ + 1 mol/l HCl in 25 ml volume.

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