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Short Communication

Substituted pyrimidinethiols as spectrophotometric reagents for osmium

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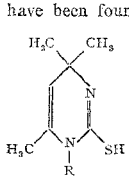
Abstract

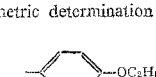
1-Phenacyl- and 1-cyclohexyl-4, 4, 6-trimethyl-1H, 4H-2-pyrimidinethiols react with Os(VIII) to form coloured complexes suitable for spectrophotometric determination of the metal. The complexes are stable, obey Beer's law and contain metal and the thiol in 1 : 3 ratio. The reactions are quite selective and many foreign ions including some of the iron and platinum group metals do not interfere.

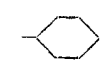
Key words: 1-Phenyl-4, 4, 6-trimethyl-1H, 4H-2-pyrimidinethiol, 1-cyclohexyl-4, 4, 6-trimethyl-1H, 4H-2-pyrimidinethiol, osmium, spectrophotometric determination.

1. Introduction

In continuation of our studies[1–3] on 1-substituted-4, 4, 6-trimethyl-1H, 4H-2-pyrimidinethiols as analytical reagents, 1-phenacyl (I) and the saturated 1-cyclohexyl (II) derivatives have been found useful for spectrophotometric determination of osmium.



(I) R = 

(II) R = 

Pink coloured osmium complex with (I) is not extractable in organic solvents while the blue complex formed with (II) gets partially extracted in chloroform, carbon tetrachloride or benzene and completely in *n*-butanol. The former complex has been studied in 50% ethanolic medium and the latter, after extraction, in *n*-butanol.

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2. Experimental

The thiols were prepared by the method of Mathes[4] and melted at 192° (I) and 147° C (II). The standard solution of (I) was prepared in alcohol and that of (II) in 0·5 N HCl. OsO_4 (1 g) was dissolved in 0·5 N NaOH and standardized. All other solutions were prepared from analytical grade reagents. Doubly distilled water was used throughout the work.

The solutions of the thiols absorb only in UV region, λ_{max} lying at 235 and 275 nm (with corresponding ϵ $9·0 \times 10^3$ and $9·6 \times 10^3$) in case of (I) and at 240 nm (ϵ $1·5 \times 10^4$) in case of (II). When a few drops of either (I) or (II) are added to Os(VIII) solution and the mixture is acidified with HCl, a pink (with I) or blue (with II) coloured species result. The coloured complexes were studied spectrophotometrically and used in selective determination of micro amounts of osmium. Their characteristics are summarized in Table I. As can be seen from the study of interferences in the determination, many ions including some from iron and platinum group metals, do not interfere using either thiol (I) or (II).

Table I

Characteristics of osmium complexes with thiols (I) and (II)

Characteristic	Os-complex with thiol (I)	Os-complex with thiol (II)
λ_{max}, nm	490	490; 590
ϵ_{max}, $l.mol^{-1}.cm^{-1}$	$4·4 \times 10^3$	5×10^3; $3·8 \times 10^3$
Thiol needed for full colour development	5-molar excess over Os	30-molar excess over Os
Medium for maximal absorbance	0·1–0·8 N HCl and 50% ethanolic	In *n*-butanol from 0·1–4·0 N HCl solution
Stability of the complex, hr	6	24
Composition (Os : thiol)	1 : 3	1 : 3
Beer's law upper limit, ppm	41·0	41·0
Accurate range of determination, ppm	7·2–39·6	7·0–38·0
Sandell sensitivity, $\mu g/cm^2$	0·0434	0·038 (at 490 nm); 0·050 (at 590 nm)
Standard deviation (from 8 samples)	0·0050*	0·0035†; 0·0051‡

* Of the absorbance for 9·5 ppm of osmium.
† Of the absorbance for 19·0 ppm of osmium at 490 nm.
‡ Of the absorbance for 19·0 ppm of osmium at 590 nm.

3. Procedure

To a suitable aliquot of Os(VIII) solution, add thiol I (0·005 M in alcohol) or II (0·01 M in 0·5 M HCl) followed by alcohol (in case of I only) and HCl to maintain the desired medium (Table I). Make up the volume and measure the absorbance of the species formed with (I) at 490 mm against 50% ethanol. Extract the species formed with (II) into *n*-butanol and make up the volume with the solvent. Measure the absorbance of the extracted species at 490 or 590 nm against the solvent blank.

4 Interferences

In determination of Os, most of the common ions do not interfere but CNS^- and thiourea do. Co(II), Ni(II) (200 ppm); Fe(II) (40 ppm); Rh(III), Ir(III), Pt(IV) (10 ppm); and Pd(II) (5 ppm) can also be tolerated in determination of 9·5 ppm of Os with (I) though Ru(III) interferes. Co, Ni (800 ppm); Ru, Rh, Ir (20 ppm); and Pd (10 ppm) can co-exist in determination of 19 ppm of Os by (II) but Ag(I), Fe(II), Pd(II) and Au(III) interfere.

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