COLORIMETRIC STUDIES ON THE REACTIONS OF DIOXOURANIUM (VI) WITH 2, 4-DIHYDROXYVALEROPHENONE AND 2, 4-DIHYDROXYCAPROPHENONE

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ABSTRACT

Dioxo-uranium (VI) forms orange yellow complexes with 2, 4-dihydroxyvalerophenone and 2, 4-dihydroxycaprophenone having λ_{max} at 400 nm in the pH range 4·0–4·5 and 4·3–4·8 respectively. The composition of the complexes as 1 : 2 (metal : ligand) has been determined by continuous variation, mole ratio and the slope ratio methods. The molecular extinction coefficients of the complexes are $3·20 \times 10^2$ and $2·95 \times 10^2$ at 400 nm and the stability constants are $3·981 \times 10^5$ and $3·622 \times 10^5$ with 2, 4-dihydroxyvalerophenone and 2, 4-dihydroxycaprophenone respectively. The limit of interference due to the presence of foreign ions in the colorimetric determination of uranium has also been determined.

INTRODUCTION

A NUMBER of reagents[1-5] have been used for colorimetric studies of uranium. This communication deals with the colorimetric studies on the reactions of 2, 4-dihydroxyvalerophenone (DHV) and 2, 4-dihydroxycaprophenone (DHC) with dioxo-uranium (VI).

EXPERIMENTAL

Reagents :

DHV[6-8] and DHC were synthesized by condensing *n*-valeric/*n*-caproic acid with resorcinol in presence of anhydrous zinc chloride at 160° C and crystallised from a mixture of hexane and toluene. They were characterized by their NMR spectra in CDCl₃. The deformed triplet at $9·10 \tau$ with $J = 6·0$ Hz was assigned to methyl group of the alkyl chain and the methylene protons α to $C = O$ appeared as triplet at $7·14 \tau$; $J = 7·5$ Hz, while the rest of the methylenes appeared as multiplet at $8·0–9·10 \tau$. The multiplet at 3·50–3·75 τ stands for two aromatic protons *H*-3 and *H*-5 and a doublet at $2·40 \tau$ with $J = 9·0$ Hz for *H*-6 proton. Two D₂O exchangeable hydroxy groups appeared as multiplet at $2·90 - 3·7 \tau$ in DHC. DHV also had the same pattern of peaks except that one methylene group was less.

I.R. spectra showed strong bands at 3500 cm⁻¹ (OH), 3380 cm⁻¹ (chelated OH), 2950 cm⁻¹, 2850 cm⁻¹ and 2800 cm⁻¹ (methylenes), 1675 cm⁻¹ (C = O) and 850 cm⁻¹ (trisubstituted benzene). A solution of the reagents in 50% ethanol was used in all experiments.

Stock solution of uranium was prepared by dissolving uranyl nitrate (B.D.H., AnalaR) crystals in double distilled water. Ammonium hydroxide and acetic acid were used to prepare the buffers of different pH values. Ionic strength was maintained by adding an appropriate quantity of 1·0 M solution of sodium perchlorate. All other chemicals were of B.D.H. AnalaR grade

OBSERVATIONS AND RESULTS

DHV and DHC instantaneously form orange yellow coloured soluble complexes with dioxo-uranium (VI).

Nature of the Complexes:

Vosburg and Cooper's method[9] employed to the orange yellow solution containing 1:1, 1:2, 1:3 and 2:1 mole ratio of metal to DHV/DHC showed that the reagents form only one complex with uranium which exhibit maximum absorbance at 400 nm in the pH ranges 4·0–4·5 and 4·3–4·8 respectively.

Effect of pH and Reagent :

The uranium complexes were found to be stable in the pH ranges 4·0–5·0. Above pH 5·0 the complexes got hydrolysed resulting in the precipitation of uranium hydroxide. The complexes attained maximum colour intensity in the pH range 4·0–4·5 and 4·3–4·8 for DHV and DHC respectively. Subsequent studies have been carried out at pH 4·2 and 4·7 respectively. It was also found that about 20 fold excess of the reagents was necessary to attain the maximum colour intensity.

Composition of the Complexes:

In all the measurements requisite amounts of ethanol were added to maintain the concentration of ethanol at 25% in final dilution; pH was adjusted as mentioned above and the ionic strength was maintained at 0·1 M NaClO₄. The composition of the complexes was determined by Job's method[11], mole ratio and slope ratio methods[11,12]. The results from all the methods indicated the formation of 1:2 (metal: ligand) complexes. In mole ratio method the zero slope of the colour intensity was approached with a large excess of the reagent. It was due to the highly dissociating nature of the complexes.

Stability Constants of the Complexes :

The stability constants of the complexes were calculated from the data in molar ratio method, using the relations :

$$K = C(1 - \alpha)/(m\alpha C)^m (n\alpha C)^n \text{ and}$$

$$\alpha = (Em - Es)/Em$$

where m, n, C, α, Em and Es have their usual meanings. The stability constants were found to be $3·981 \times 10^5$ and $3·622 \times 10^5$ for DHV and DHC complexes

respectively. The standard free energy of formation ($\Delta F = - RT \ln K$) were found to be 8·301 and 7·718 Kcal mole at 30°C respectively.

Molar Extinction Coefficient and Sensitivity:

The values of molar extinction coefficients from the slope ratio curves are $3 \cdot 2 \times 10^2$ and $2 \cdot 95 \times 10^2$ at 400 nm and the sensitivities are 0·743 and 0·801 μg U cm^2 (Sandell Scale)[13] for DHV and DHC complexes respectively.

Procedure for Estimation:

The solution containing 30–85 ppm of uranium was treated with 20-fold excess of the reagents and the pH was adjusted as mentioned above. Requisite amount of ethanol was added to maintain its proportion at 25% level in final dilution and the ionic strength was maintained at 0·1 M $NaClO_4$. The absorbance was measured at 400 nm against a blank containing corresponding concentration of metal ions. From the abosrbance value, concentration of the metal ions can be evaluated with the help of the calibration curve.

Effect of Foreign Ions:

The influence of foreign ions on the estimation of uranium using DHV and DHC was also studied in the usual manner. It was observed that at 40 ppm concentration of uranium, 1000 ppm of Al (III), Ba (II) Be (II), Cd (II), Ca (II), Fe (II), Mg (II), Sr (II), K (I), Na (I), NH_4 (I), Cl$^-$, ClO_4^-, NO_3^-, SO_4^{2-}; 750 ppm of Br$^-$, Co$^-$ (II); 500 ppm of Cr (III), Pb (II), Ag (I), Mn (II), Ni (II); 150 ppm of I$^-$, Tl (I) could be tolerated. However, Cu (II), Fe (III) and Pd (II) interfere at all levels. These must be eliminated prior to estimation.

Structure of the Complexes:

The structures of the complexes have been proposed on the basis of I.R. spectra. The spectral data for the ligands and the complexes indicate that most of the frequencies are perturbed on complex formation. I.R. spectrum of the ligand shows two bands in OH stretch region assigned to two different types of hydroxyl groups present in the ligand. The band at 3450 cm^{-1} remains unaffected on complexation, hence it may be due to the 4-hydroxy group. The position of the second band (3330 cm^{-1}) and its disappearance in the spectra of the complexes shows that it may be due to the presence of an intramolecularly hydrogen bonded OH at position-2 in the ligand. The co-ordination of the keto group through oxygen is indicated by the lowering of C = O band from 1675 cm^{-1} in the ligand to the range 1625 cm^{-1} in the complexes. The U = O band appears at 920 cm^{-1}.

Appearance of new band at 555 and 560 cm^{-1} is fairly attributed to metal oxygen bands. On the basis of the above evidence, the following structure (I) may be assigned to the complexes:

M = O = U = O
R = − C_4H_9, C_5H_{11}
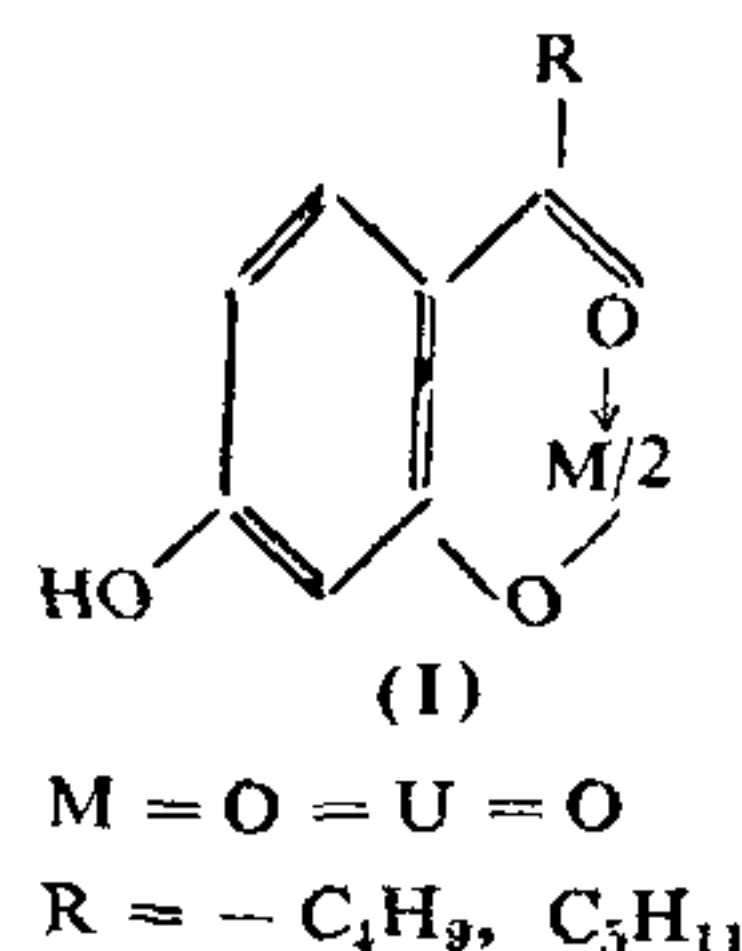
The results presented above show that DHV and DHC are good reagents for uranium. The method is rapid and reliable and the reagents can be used in acidic medium so that the metal hydroxides are not precipitated. Despite the inductive effect of alkyl chain attached to the carbonyl carbon and hydroxyl group at position-4 in the ligand which increase the stability of the complexes by increasing the basic streng)h of the ligands, the overall steric effect of the bulkier group (solvation effect) decreases the stability of the DHC complex.

1. Gupta, B. D. and Malik, W. U., *J. Ind. Chem. Soc.*, 1970, **47** (2), 145.

2. Desai, M. N. and Desai, B. M., *Curr. Sci.*, 1965, **34**, 244.

3.. Poddar, S. N., *Ind. J. Appl. Chem.*, 1964, **27**, 67.

4. Urs, M. K. and Neelkantam, K., *J. Sci. Ind. Res.*, 1952, **11 B**, 79.

5. Singh, J. and Gupta, S. P., *Curr. Sci.* (in press).

6. Nogami, H., *J. Pharm. Soc. Japan*, 1941, **61**, 46.

7. Singh, J., Gupta, S. P. and Malik, O. P., *Ind. J. Chem.*, 1975, **13**, 1217.

8. Dohme, A. R. L., Cox, E. H. and Ellis Miller, *J. Am. Chem. Soc.*, 1926, **43**, 1688.

9. Vosburg, W. C. and Cooper, G. P., *Ibid* 1941, **63**, 437.

10. Job, P., *Ann. Chim.*, 1928, **9**, 113.

11. Yoe J. H. and Jones, A. L., *Ind. Eng. Chem. Anal. Ed.*, 1944, **16**, 111.

12. Harvey, A. E. and Manning, D. L., *J. Am. Chem. Soc.*, 1950, **72**, 4488.

13. Sandell, E. B., *Colorimetric Determination of Traces of Metals* (Interscience Publications, Inc., New York), 1959, pp. 83, 97.