# bis (2-Hydroxy-5-methyl acetophenone oximato) dioxo Molybdenum (VI)

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Spectrophotometric and conductometric methods have been employed to study the nature, composition and stability of Mo(VI)-2-hydroxy-5-methyl acetophenone oxime. The complex is bright-yellow in colour and stable over the $p$H range 2·0–5·0.

Vos Burgh and Cooper's method demonstrates the existence of only one complex having the maximum absorption at 345 m$\mu$. The stoichiometric ratio of molybdenum and the ligand has been determined to be 1 : 2 in this complex. Its formation constant has been found to be $4·87 \times 10^8$ while $\Delta F°$ be $-12$ Kcal. /mole at 30°.

The results of chemical analysis of pure, dry sample of the isolated complex reveal its molecular formula $(C_9H_{10}O_2N)_2MoO_2$. A structure has been assigned to the complex.

The metal complexes of ortho-hydroxy aryl aldoximes have been used mainly for the detection and determination of the respective metals. For example, Salicylaldoxime[1] forms an insoluble complex with copper and is employed for the gravimetric determination of this metal. Ortho-hydroxy acetophenone oxime[2] forms both soluble and insoluble complexes with a number of metal ions and has been recommended for the determination of these ions.

Preliminary experiments have revealed that 2-hydroxy-5-methyl-acetophenone oxime reacts with molybdenum(VI) in acidic media, giving yellow coloured, soluble complex. The reaction is instantaneous. The nature, composition and stability of this complex, have been determined in the present investigation.

## EXPERIMENTAL

*Apparatus* : Absorbance measurements were carried out with a Unicam Spectrophotometer, model SP 500, whilst a Beckman $p$H-meter, model H, was used for $p$H measurements. Conductance measurements were made with a Philip's (PR 9500) conductivity bridge, using a dip-type conductivity cell.

*Solutions* : A pure sample of 2-hydroxy-5-methyl accetophenone was prepared by the Fries migration[3] of $p$-cresyl acetate in the presence of anhydrous aluminium chloride. Its oxime was prepared by the action of hydroxylamine hydrochloride and sodium acetate. The product was purified by repeated crystallization. Its solution was prepared in 50% alcohol.

1. F. Ephraim, *Ber.*, 1930, **63B**, 1928.

2. S. N. Poddar, *Z. Anal. Chem.*, 1957, **154**, 254.

3. A. Vogel, A Text-Book of Practical Organic Chemistry, 3rd Ed., Longmans, Green and Co., London, p. 676.

A stock solution of molybdenum (approx. $0.02M$) was prepared by dissolving ammonium molybdate (E. Merck) in doubly-distilled water and standardizing gravimetrically.

## RESULTS AND DISCUSSION

Molybdenum (VI) reacts instantaneously with 2-hydroxy-5-methyl acetophenone oxime (H.M.A.O.) in the acidic media to form a stable, bright-yellow, soluble complex.

The nature and composition of the complex has been ascertained, employing spectrophotometric and conductometric methods.

*Spectrophotometric Studies :* Vosburgh and Cooper's method[4] shows the existence of only one complex in the yellow solution since the equimolar solutions containing Mo(VI) and H.M.A.O. in different proportions, exhibit only one absorption maxima at 345 m$\mu$ (Fig. 1).
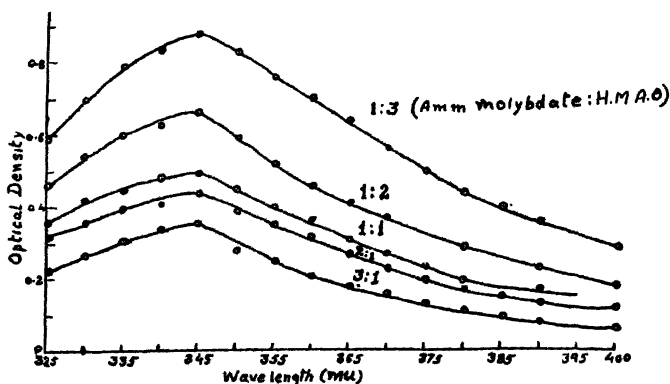


*Fig. 1.* VOSBURGH- COOPER's method.
Absorption spectra of the mixtures of amm. molybdate and H.M.A.O. in different proportions.

The influence of $pH$ on this colour reaction was studied by measuring the absorbance of Mo(VI) and H.M.A.O. mixture (1 : 2) solutions at different $pH$ values. The solutions in the $pH$ range 2.0–5.0 attained the maximum absorption at 345 m$\mu$ ($\lambda_{max}$ of the complex), showing thereby that the complex is stable in this $pH$ range.

Preliminary studies on the effect of temperature on the colour intensity of the solution showed that the colour was stable upto 40°; beyond that temperature the colour started fading away. However, the solution regained its original colour intensity on cooling to 40° or below.

Job's method of continued variation[5] was employed to determine its composition. Equimolar solutions were prepared by mixing Mo(VI) and H.M.A.O. in varying proportions

4.   W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.

5.   P. Job, *Ann. Chim.*, 1928, 9(10), 113.

and their optical density was measured at 345 m$\mu$.   The difference between the optical density of the mixture and H.M.A.O. solutions was plotted against the mole fraction of Mo(VI) (Fig. 2).   The maximum deviation occurred at the ratio of 1 : 2 of Mo(VI)  and H.M.A.O.
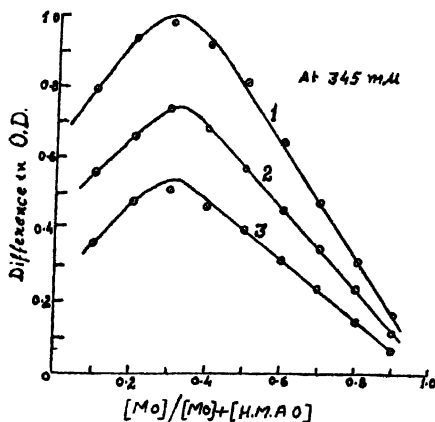


Fig. 2. Job's method of continued variation.
Curve 1, conc. 1·333×10⁻³ M  ;  Curve 2, conc.
1×10⁻³ M ;   Curve 3, conc. 8×10⁻⁴ M

Slope Ratio method[6] extended further support to the results of Job's method.   Fig. 3 shows the absorbance data at 345 m$\mu$, plotted against the concentration of the variable
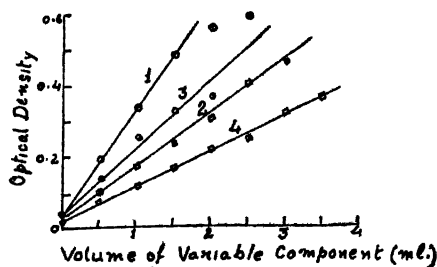


Fig. 3. Slope ratio method.
Curves 1,3, amm. molybdate varyings
Curves 2,4,  H.M.A.O. varying.

content.   The ratio of the slopes of straight line portions of these  curves  confirms the existence of 1 : 2 complex.

6.   A. Harvey and D. Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.

*Conductometric Studies* : Fig. 4 shows the conductometric titration curves of ammonium molybdate against H.M.A.O. The inflexion points correspond to 1 : 2 complex of Mo(VI) with H.M.A.O.
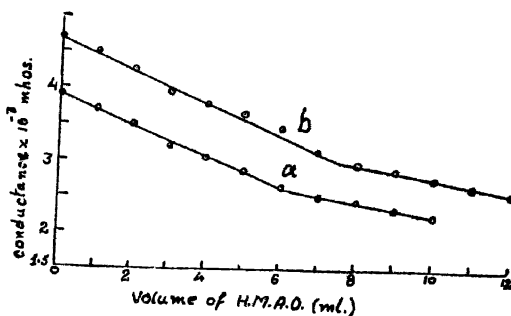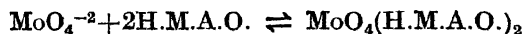


Fig. 4. Conductometric titrations.
30 ml. solutions of $2 \times 10^{-3}$ M (curve a) and $2.66 \times 10^{-3}$ M (curve b) amm. molybdate titrated against $2 \times 10^{-2}$ M H.M.A.O.

*Formation Constant of the Complex* : Anderson's modified method as adopted by Dey and coworkers[7], was applied for determining its formation constant. For the reaction

$$MoO_4^{-2} + 2H.M.A.O. \rightleftharpoons MoO_4(H.M.A.O.)_2$$

if $x$ represents the concentration of the complex at equilibrium and $a$ and $b$, the initial concentrations of $MoO_4^{-2}$ ions and H.M.A.O. respectively, the formation constant of the complex is given by :

$$K = \frac{x}{(a-x)(b-2x)^2} \qquad \text{(i)}$$

Taking two values of $a$ and $b$ for the solutions showing the same absorbance i.e., the same value of $x$, we have

$$K = \frac{x}{(a_1-x)(b_1-2x)^2} = \frac{x}{(a_2-x)(b_2-2x)^2} \qquad \text{(ii)}$$

The value of $x$ can be calculated and consequently the value of $K$ by substituting the value of $x$ in equation (i). The absorbance of the mixture solution in the Job's method of continued variation, was plotted against $(MoO_4^{-2})/(MoO_4^{-2})+(H.M.A.O.)$. An arbitrary absorbance value of 0·19 was chosen and the initial concentrations of the reactants were read from the graph in the descending portions of the curves (Fig. 5). The value of $K$ was calculated to be $4·87 \times 10^8$. The free energy of formation $\Delta F°$ was also determined from the relationship $\Delta F° = -RT \ln K$ and found out to be $-12·0$ Kcal./Mole.

7.   A. Mukherji and A. Dey, *J. Ing. Nucl. Chem.*, 1958, 6, 314; *Anal. Chim. Acta.*, 1958, **18**, 324.

The complex was isolated and analysed for its molybdenum and nitrogen contents. From the results of the analysis, the molecular formula of the complex was determined as $(C_9H_{10}O_2N)_2MoO_2$.
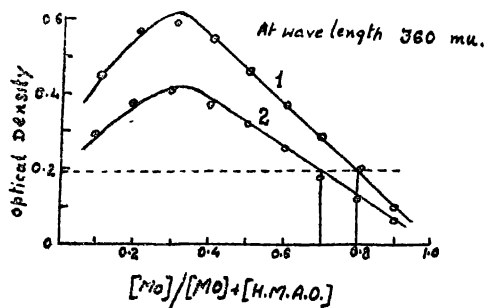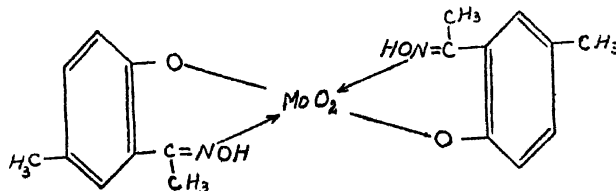


Fig. 5. Formation constant of the complex. Conc. of reactants: $1 \times 10^{-3}$ M (solution 1) and $8 \times 10^{-4}$ M (solution 2)

From the known constitution of metal-o-hydroxy acetophenone oxime compounds[8], the molybdenum(VI)-2-hydroxy-5-methyl acetophenone-oxime may be represented by the following structure :—

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8.   B. D. Gupta and W. U. Malik, *J. Less. Common Metals*, 1969, **17**(3), 277.