

and copper(II) (2 fold) did not interfere in the determination. Higher amounts of copper could be tolerated if toluene is added to butanol. Nickel(II), vanadium(V) and tungsten(VI) interfere if their concentration exceeds twice that of iron.

The Coleman⁵ graphical analysis of the organic layer showed that only a single species of the complex is extracted. The results obtained in Job's method applicable to two phase system, indicated that the metal to ligand ratio is 1:1. This is further confirmed by log-log plot. The stability constant of the complex calculated from the data obtained in the Job's method is 7.4×10^4 .

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GENERAL SPRAY REAGENTS FOR NATURALLY OCCURRING HIGHER FATTY ACIDS AND THEIR METHYL AND ETHYL ESTERS

MANY spray reagents have been in use for detecting the presence of fatty acids and their methyl and ethyl esters¹⁻³. Since these reagents very often do not produce pronounced colour, it was considered necessary to search for the sensitive spray reagents suitable for detecting the presence of fatty acids and their methyl and ethyl esters. This was achieved by paper chromatographic procedures involving the use of Whatman No. 1 filter-paper, impregnated with 2% solution of olive oil in benzene⁴, and 90% ethanol as the developing solvent. The developed chromatograms were dipped in 1% solution of curcumin, whereupon the chromatograms became yellow. The yellow chromatograms were then dipped in (1) 10% aqueous caustic soda solution or (2) 10% aqueous sodium arsenite solution or (3) 10% aqueous potassium ferrocyanide solution or (4) benedict's solution (BDH) or

(5) saturated solution of borax whereupon the colour of the chromatograms changed to reddish brown but the colour of the spots of fatty acids and their esters remained yellow, probably due to adsorption of curcumin. The colour of the spots became more pronounced after the chromatograms were dried in air. The R_f values are: oleic acid 0.04, stearic acid 0.16, palmitic acid 0.21, myristic acid 0.52, ethyl oleate 0.28, ethyl-stearate 0.87, methyl palmitate 0.85 and ethyl myristate 0.32.

The above paper chromatographic procedure has successfully been extended to the quantitative estimation of the fatty acids and their esters in a klett-summerson photoelectric colorimeter using blue filter (420 nm) with the help of standard curves of authentic acids and their esters. Two sets of standard solutions of mixture of (1) oleic acid, stearic acid, myristic acid, ethyl myristate and methyl palmitate (20 mg each in the same 100 ml ethanol) and (2) palmitic acid, ethyl oleate, ethyl stearate (20 mg each in the same 100 ml ethanol) were prepared and 0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml and 1.0 ml of each set containing 40, 80, 120, 160, 200 μ g of each compound present in the above two sets of mixtures were chromatographed and the colour was developed by making use of the above spray reagents. The coloured spots were cut out and eluted by immersing in methanol (5 ml each) and the colour intensity of each eluate measured. The concentration of oleic acid, stearic acid, myristic acid, ethyl myristate, methyl palmitate, palmitic acid, ethyl oleate and ethyl stearate were found to be 86%, 82%, 85%, 84%, 86%, 82%, 83% and 85% respectively of the theoretical value from the standard curves.

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TERPENIC KETONES AS CHELATING LIGANDS: SPECTROPHOTOMETRIC INVESTIGATION ON VANADIUM (IV) COMPLEX WITH α -CYCLOCITRYLIDINE ACETONE

THE metal complexes of terpenic ketones have not been investigated so far. A review of literature shows that metal complexes of α -cyclocitrylidine

acetone have not been reported by earlier workers. This communication deals with the interaction of vanadium IV with α -cyclocitrylidine acetone where oxygen of carbonyl group and π -allylic bond of the ligand molecule offer coordination sites.

Experimental

Standard solutions of α -cyclocitrylidine acetone and vanadyl sulphate (monohydrate, B.D.H.) were prepared in ethanol and distilled water respectively. Concentration of vanadyl sulphate solution was further checked gravimetrically¹. Fresh solutions of the metal and the ligand were prepared before use. Absorbance measurements were carried out with Baush and Lomb Spectronic-20 colorimeter. The pH of the solution was adjusted by the addition of ammonia-ammonium chloride buffer.

Results and Discussion

Intensity of the colour developed increases with time and attains a maximum in about one hour. Hence, all the measurements were made one hour after mixing of the solutions.

Vosburgh and Cooper's method² was employed to determine the nature of the complex formed. Reactants were mixed in different stoichiometric ratios and the absorbance of each mixture was measured at suitable wavelengths within the range of 320 m μ to 600 m μ . The maximum absorbance was found to be at 550 m μ for the complex and at pH 6.0. This indicates that only one complex with λ -max. 550 m μ is formed under the specified conditions.

The composition of the complex was established by Job's continuous variation method³ and molar ratio method⁴. The results indicate that vanadium(IV) forms 1 : 1 complex with the ligand. VO (C₁₃H₂₀O). Results were further confirmed by the elemental analysis of the isolated complex:

Calc.: C-60.2%, H-7.71%, Found: C-60.1%, H-7.74%

Effect of pH: Several mixtures containing vanadyl sulphate and the reagents in the ratio of 1 : 1 were prepared, pH was adjusted to different values and their absorbance was measured at different wavelengths. The results show that λ -max of the complex (550 m μ) occurs between pH 5.2-7.5. It is hence the pH at which the complex was stable.

The apparent stability constant was calculated by Dey and Mukerjee's method⁵ using Job's curve and was found to be $7.6 \pm 0.1 \times 10^4$. The corresponding free energy of formation of the complex is 6.59 ± 0.01 K. cal at 25° C.

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PREPARATION OF 2:4-DIHYDROXY 5-ACETYL ACETOPHENONE (RESODIACETOPHENONE)

SEVERAL methods have been reported in literature for the preparation of 2:4-dihydroxy acetophenone (resacetophenone). Some of these are by heating resorcinol with (a) ZnCl₂ and acetic acid^{1,2}, (b) ZnCl₂ and acetic anhydride², (c) ZnCl₂ and acetyl chloride³, (d) BF₃ and acetic anhydride⁴, (e) AlCl₃ and acetyl chloride⁵.

In our attempts to prepare it by heating resorcinol with ZnCl₂ and acetic anhydride no resacetophenone, could be obtained. On the other hand, a different reddish brown product was obtained in 96.5% yield. It was recrystallised from benzene or methanol using norit to give colourless crystals, m.p. 178-80° C, analysing for C₁₀H₁₀O₄. From its m.p. and molecular formula, the product appeared to be identical with 2:4-dihydroxy 5-acetyl acetophenone (resodiacetophenone), which has been prepared earlier by one of the following methods:

- (i) by the treatment of resacetophenone with glacial acetic acid and POCl₃⁶.
- (ii) by the treatment of resorcinol diacetate with ZnCl₂⁷ or
- (iii) by heating dry distilled resorcinol diacetate and sublimed FeCl₃ at 180° C in an atmosphere of CO₂⁸.

The identity of the compound obtained was further confirmed by comparing its derivatives: diacetate⁹, m.p. 120° C and dibenzoate⁹, m.p. 118° C. The above method thus forms an elegant one step synthesis of 2:4-dihydroxy 5-acetyl acetophenone from resorcinol.