

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 $m\mu$ to 600 $m\mu$. The maximum absorbance was found to be at 550 $m\mu$ for the complex and at pH 6.0. This indicates that only one complex with λ -max. 550 $m\mu$ 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 ($C_{13}H_{20}O$). 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 $m\mu$) 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.

Authors are thankful to the Director, C.D.R.I., Lucknow, for the elemental analysis, and also wish to express their gratitude to C.S.I.R., New Delhi for

the award of fellowship to (M.A.) and State C.S.I.R., Lucknow, for the award of fellowship to (R.G.).

Chemistry Department, MISS MAMTA AGRAWAL.
Govt. Razza P.G. College, RAMESH GUPTA.
Rampur-244 901, India. R. K. BASLAS.*
July 14, 1978.

*Chem. Dept., M.B.P.G. College, Haldwani-263139, U.P., India.

1. Furman, N. H., *Standard Methods of Chemical Analysis*, D. Van Nostrand Co., Princeton 1962, 1, Ed., 6, 1210.
2. Vosburgh, W. C. and Cooper, G. R., *J. Am. Chem. Soc.*, 1941, 63, 437.
3. Job, P., *Ann. Chem.*, 1928, 9, 113.
4. Yol, J. H. and Jones, A. L., *Ind. Eng. Chem. Analyt.*, Ed; 1944, 16, 111.
5. Mukerjee, A. K. and Dey, A. K., *I, Inorg. Chem. and Nucl.*, 1958, 6, 314; *Anal. Chim. Acta*, 1958, 18, 324.

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) $ZnCl_2$ and acetic acid^{1,2}, (b) $ZnCl_2$ and acetic anhydride², (c) $ZnCl_2$ and acetyl chloride³, (d) BF_3 and acetic anhydride⁴, (e) $AlCl_3$ and acetyl chloride⁵.

In our attempts to prepare it by heating resorcinol with $ZnCl_2$ 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 $C_{10}H_{10}O_4$. 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 $POCl_3$ ⁶.
- (ii) by the treatment of resorcinol diacetate with $ZnCl_2$ ⁷ or
- (iii) by heating dry distilled resorcinol diacetate and sublimed $FeCl_3$ at 180° C in an atmosphere of CO_2 ⁸.

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.

EXPERIMENTAL

To a mixture of freshly fused and powdered $ZnCl_2$ (10g.) in dry acetic anhydride (14 ml) contained in a conical flask dry resorcinol (10 g.) was added quickly while stirring. The mixture was gently heated on a flame to $142^\circ C$ (15 mts.). The viscous red solution was allowed to cool to room temperature. 80 ml. of HCl (1:1) were added to syrupy mass and stirred. After a few minutes an orange-red crystalline material separated out. The crude product (17 g., 96.5%) was crystallised twice from methanol using norit to give 2:4-dihydroxy 5-acetyl acetophenone (resodiacetophenone) as colourless crystalline solid (Yield 90%, m.p. $178-80^\circ C$).

Found : C, 61.65; H, 5.25. $C_{10}H_{10}O_4$ requires C, 61.80; H, 5.15% Resodiacetophenone diacetate : (Acetic anhydride in pyridine at room temperature for 24 hrs.) m.p. $120^\circ C$ (Lit⁹ m.p. $120^\circ C$) Resodiacetophenone dibenzoate : (Benzoyl chloride in Pyridine) m.p. $118^\circ C$ (Lit⁹ m.p. $118^\circ C$).

Department of Chemistry, A. S. R. ANJANEYULU,
 Andhra University, A. V. RAMA PRASAD,
 Waltair, D. SIVAKUMAR REDDY.
 October 3, 1979.

1. Robinson, R. and Shah, R. C., *J. Chem. Soc.*, 1934, p.1491.
2. Nencki, M. and Sieber, N., *J. Prakt. Chem.*, 1881, 23 (2), 147.
3. Eijkman, *Chem. Weekblad*, 1904, 1, 453; *Chem. Zentr.*, 1904, 75, II, 1597.
4. Killelea, J. R. and Lindwall, H. G., *J. Am. Chem. Soc.*, 1948, 70, 428.
5. Desai, R. D. and Ekhlal, M., *Proc. Indian Acad. Sci.*, 1938, 8A, 194.
6. Torrey, H. A. and Kipper, H. B., *J. Am. Chem. Soc.*, 1908, 30, 850.
7. Eijkman, *Centr.*, 1904, I, 1597; 1905, I, 814.
8. Heller, *Ber.*, 1912, 45, 418.
9. Heilbron, I. Ed., *Dictionary of Organic Compounds.*, 1965, 2, 848.

**ACID PHOSPHATASE ACTIVITY IN
 COTYLEDONS OF GERMINATING SEEDS
 OF *VIGNA SINENSIS* (LINN.) SAVI**

ON the basis of the extensive studies of the developmental patterns of alkaline and acid phosphatases of avian embryos, it was suggested that acid phosphatases which remain at relatively constant level of activity during the growth of the chick embryo, function as constitutive enzymes whereas alkaline phosphatases which show marked fluctuation in the level and locus of activity, function as adaptive enzymes^{1,2}. However, the developmental patterns of the phosphatases of growing plants are in contrast with those of the chick embryo. The activity of acid phosphatase at various hours of germination increases with time.

The present investigation is mainly concerned with the development of acid phosphatase activity in the cotyledons (half-seeds without embryo) at various times of germination. Also, we report here the presence of multiple forms of acid phosphatase as separated by polyacrylamide gel electrophoresis and subsequently stained by the α -naphthyl phosphate and "fast" blue RR³.

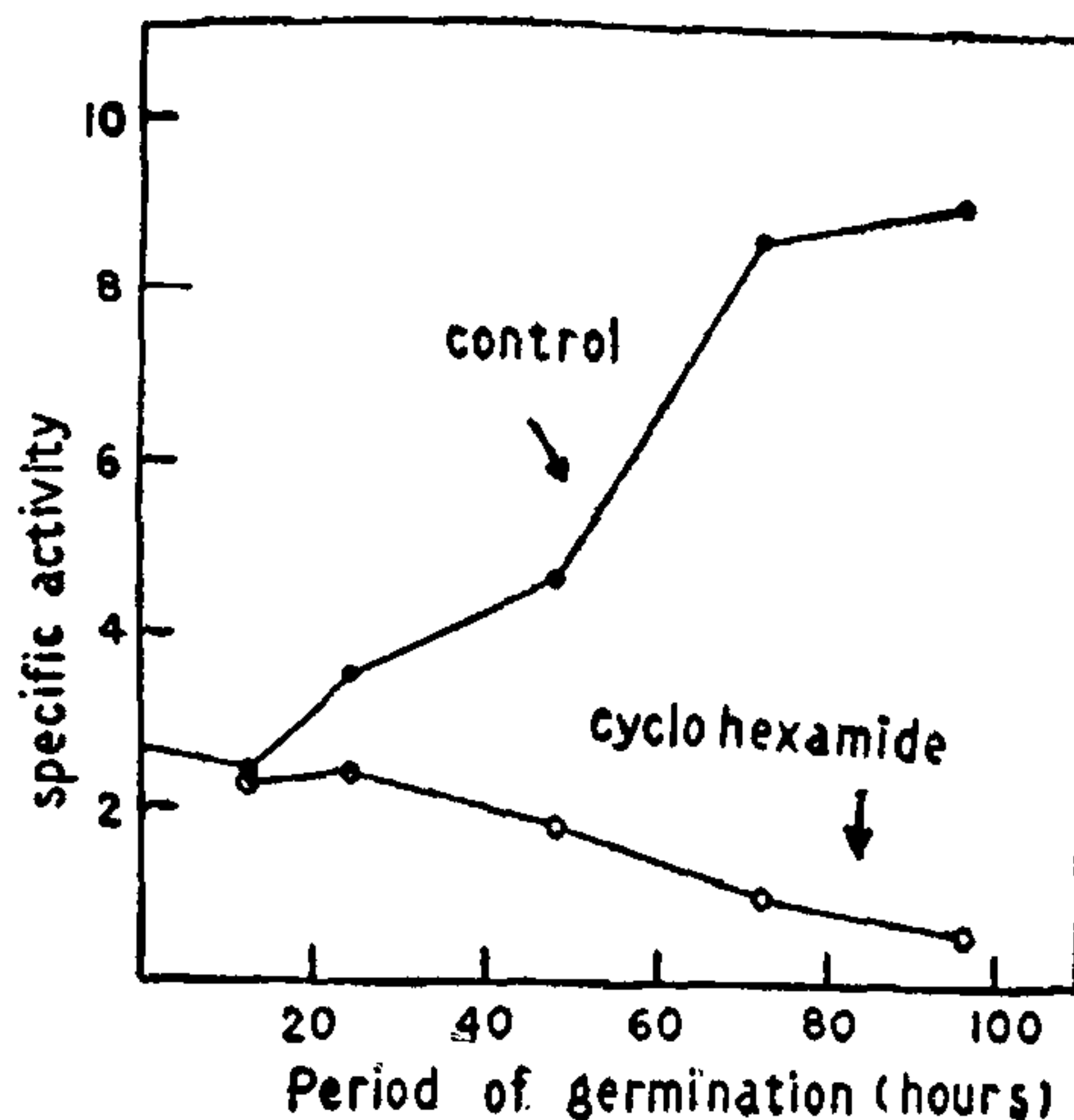


FIG. 1. Acid phosphatase activity as measured by *p*-nitrophenol method (4) at various hours of germination at $28^\circ C$. Control: After imbibition whole seeds were broken into half seeds and the half seeds without embryo were kept under germinating conditions at $28^\circ C$.

In another set half seeds without embryo were kept in germinating conditions with cyclohexamide solution (100 $\mu g/ml$). Cotyledons were homogenized as described in legends of Fig. 2 and the homogenate was then centrifuged at $3,000 \times g$ for 10 min at $4^\circ C$. The Cell-free extract was then used as enzyme source. Specific activity has been defined as μ mole of *p*-nitrophenol liberated/mg protein/hr.

The results given in Fig. 1 indicate that the acid phosphatase activity (as measured using *p*-nitrophenyl phosphate as substrate⁴) increases with the increase in time after imbibition of the half seeds (without embryo) at $28^\circ C$. The rate of increase of acid phosphatase activity in the half-seeds is maximum in 48-60 hrs. However, the acid phosphatase activity has been found to decrease when the seeds were kept in cyclohexamide solution (100 $\mu g/ml$) after 2 hrs of imbibition at $28^\circ C$. The results given in Fig. 1 suggest that the increase in the acid phosphatase activity in the cotyledons, kept under germinating condition is mainly due to the *de novo* synthesis of the