

This is attributed a decrease of the (N=O) double bond character as a result of selenium-oxygen coordination. This observation is in agreement with the pyridine N-oxide and related ligand complexes with various acceptor molecules<sup>5,11</sup>. Coordination of PhenO<sub>2</sub> to phosphorus atom of P<sub>4</sub>Se<sub>3</sub> leads to the shift of  $\nu(\text{NO})$  1269 and 1249 cm<sup>-1</sup> (bending) and  $\delta(\text{NO})$  811 and 808 cm<sup>-1</sup> (stretching) to the lower spectral regions. It is further supported by the lowering of the ring stretching vibration on coordination.

The exocyclic P = Se stretching frequency<sup>12</sup> appears to be slightly shifted to the upper region indicating that the double bond character of the P = Se bond is decreased. The skeletal P-Se-P stretching vibrations are observed at the lower region. The asymmetric and symmetric P-Se-P skeletal stretching vibrations are observed at 420 and 405 cm<sup>-1</sup> in the case of pyridine adduct, at 412 and 398 cm<sup>-1</sup> in the case of pyridine N-oxide and in case of adducts of PhenO<sub>2</sub> and BipyO<sub>2</sub>, these bands are observed at 420, 408 and 420, 412 cm<sup>-1</sup> respectively. In addition the absence of selenium-nitrogen or selenium-oxygen bond and the appearance phosphorus-nitrogen or phosphorus-oxygen band in the region 750-780 cm<sup>-1</sup>, not present in the parent compounds, suggests that phosphorus atom is the acceptor.

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1. Mai, J., *Ber. Deut. Chem. Ges.*, 1927, **60**, 222.
2. Marono, V. A. and Schaslok, R. Y., *J. Inorg. Nucl. Chem.*, 1971, **33**, 3182.
3. Panney, G. J. and Scheldrick, G. M., *Acta Cryst.*, 1970, **26**, 2095.
4. Gill, N. S., Nuttal, R. H., Scaife, D. S. and Sharp, D. W. A., *J. Inorg. Nucl. Chem.*, 1961, **18**, 79.
5. Kida, S., Quagliano, J. V., Walmsley, J. A. and Tyree, S. Y., *Spectrochim. Acta*, 1963, **19**, 189.
6. George, J. W., Katsaros, N. and Wynne, K. J., *Inorg. Chem.*, 1967, **6**, 903.
7. Paul, R. C., Makhni, H. S., Singh, P. and Chadha, S. L., *J. Less. Common Metals*, 1963, **17**, 437.
8. Paul, R. C., Khurana, H., Vasisht, S. K. and Chadha, S. L., *J. Ind. Chem. Soc.*, 1969, **46**, 915.
9. Dusig, J. R., Layton, R., Sink, D. W. and Mitchell, B. R., *Spectrochim. Acta*, 1965, **2**, 1367.

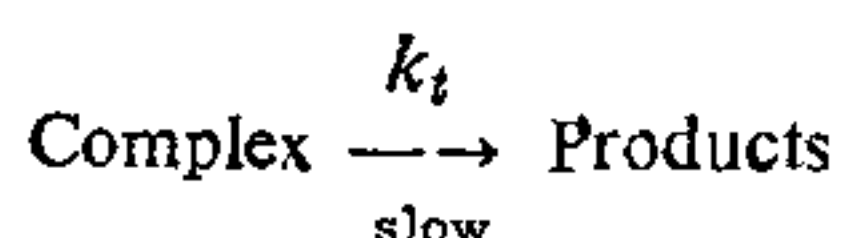
10. Malhotra, K. C. and Krishan, B., *J. Inorg. Nucl. Chem.*, 1977, **39**, 1523.
11. Quagliano, J. V., Fujita, J., Franz, G., Philips, D. J., Walmsley, J. A. and Tyree, S. Y., *J. Am. Chem. Soc.*, 1961, **83**, 3770.
12. Zingaro, R. A., *Inorg. Chem.*, 1963, **2**, 192.

#### MICELLAR CATALYZED Ce(IV)-ACETONE REACTION

MICELLAR catalysis is a field of current research interest and oxidation reaction catalyzed by micelles has not been studied so far. Hence it is proposed to choose an oxidation reaction to investigate micellar effects. In the present study, oxidation of acetone by Ce(IV) is subjected to micellar catalysis. Since this reaction involves a neutral substrate and a positively charged oxidant, an anionic surfactant is expected to catalyze the reaction. Sodium dodecyl sulphate (SDS), the well-known anionic surfactant has been chosen as the catalyst for the oxidation reaction.

The uncatalysed oxidation reaction has been reported in literature<sup>1,2</sup> as proceeding *via* two distinct steps obeying Michaelis-Menten kinetics.

K



It is of interest to study the micellar-catalyzed reaction in order to find out whether the equilibrium constant K for complex formation or the rate constant  $k_t$  for the decomposition of the complex is affected since an increase in either K or  $k_t$  may lead to rate acceleration.

Experiments have been carried out under pseudo-first-order conditions with [acetone]  $\gg$  [Ce(IV)], [Ce(IV)] = 3 - 4  $\times$  10<sup>-4</sup> mol. dm<sup>-3</sup> [acetone] = 0.17 to 0.50 mol. dm<sup>-3</sup>, [HClO<sub>4</sub>] = 1.0 mol. dm<sup>-3</sup> and ionic strength,  $\mu$  = 1.0 mol. dm<sup>-3</sup> at 30°C. For the micellar-catalyzed reaction, the concentration of SDS is chosen as 1.35  $\times$  10<sup>-3</sup> mol. dm<sup>-3</sup>, one of the reported values<sup>3</sup> of critical micelle concentration (CMC) of sodium dodecyl sulphate. The uncatalyzed oxidation has been followed by titrimetry and the micellar reaction by spectrophotometry, the optical density measurements being made at 420 nm. Under the experimental conditions, there is no oxidation of the surfactant by Ce(IV).

Sodium dodecyl sulphate catalyzes the oxidation of acetone by Ce(IV) in accordance with expectation. The pseudo-first-order rate constants  $k_0$ , s<sup>-1</sup> and  $k_\psi$ , s<sup>-1</sup> for the uncatalyzed and micellar reactions respectively have been evaluated at different [acetone] and it is found to be in the order,  $k_\psi > k_0$ . The double

reciprocal plots of  $k_0^{-1}$  or  $k_{\psi}^{-1}$  vs  $[\text{acetone}]^{-1}$  have been found to be linear with intercept on the ordinate indicating that both the uncatalyzed and micellar-catalyzed oxidations proceed *via* complex formation obeying Michaelis-Menten kinetics. The rate law is therefore of the form,

$$\frac{1}{k_0} \text{ or } \frac{1}{k_{\psi}} = \frac{1}{k_t} + \frac{1}{k_t K [\text{acetone}]}$$

The values of  $k_t$  and  $K$  have been evaluated from the intercept and slope of the Michaelis-Menten plots. The value of  $k_t$  is found to be  $4.7 \times 10^{-4} \text{ s}^{-1}$  for the uncatalyzed as well as the micellar reaction. But  $K$  is found to be greater for the micellar reaction,  $K = 2.1 \text{ mol}^{-1} \text{ dm}^3$  for the uncatalyzed Ce(IV)-acetone reaction and  $K = 2.7 \text{ mol}^{-1} \text{ dm}^3$  for the micellar-catalyzed oxidation. These data show clearly that the rate acceleration is due to an increase in equilibrium constant for complex formation, *i.e.*, the stability of Ce(IV)-acetone complex is increased, in presence of micelles.

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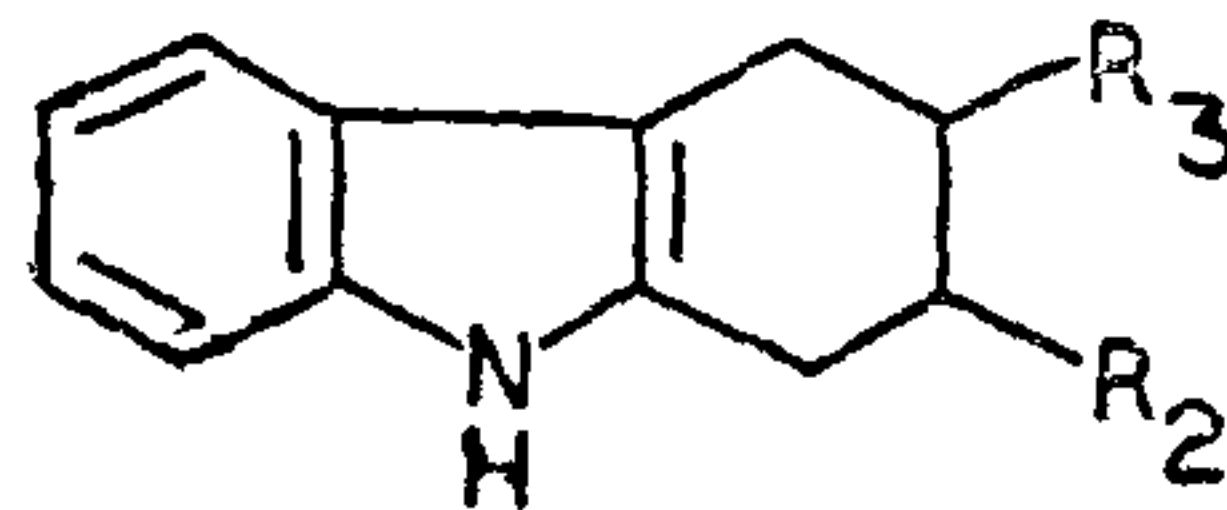
MEENAKSHI MARUTHAMUTHU,  
G. USHA,

- Shorter, J. and Hinshelwood, S. C., *J. Chem. Soc.*, 1950, p. 3276.
- Venkatakrishnan, S. and Santappa, M., *Z. Phys. Chem.*, 1958, 16, 73.
- Bennion, B. C., Tong, L. K. J., Holmes, L. P. and Eyring, E. M., *J. Phys. Chem.*, 1969, 73, 3288.

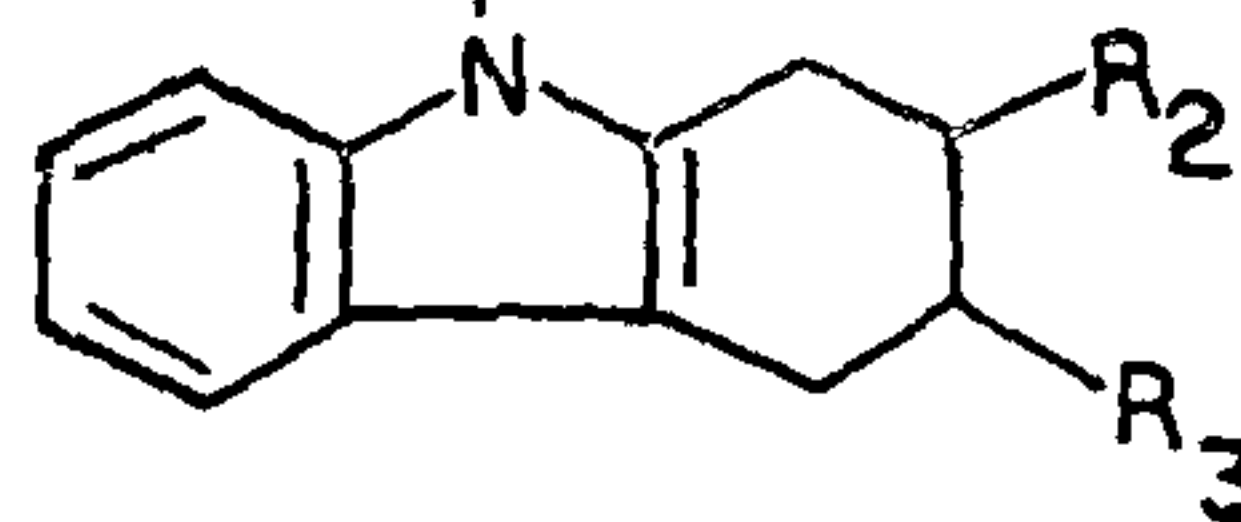
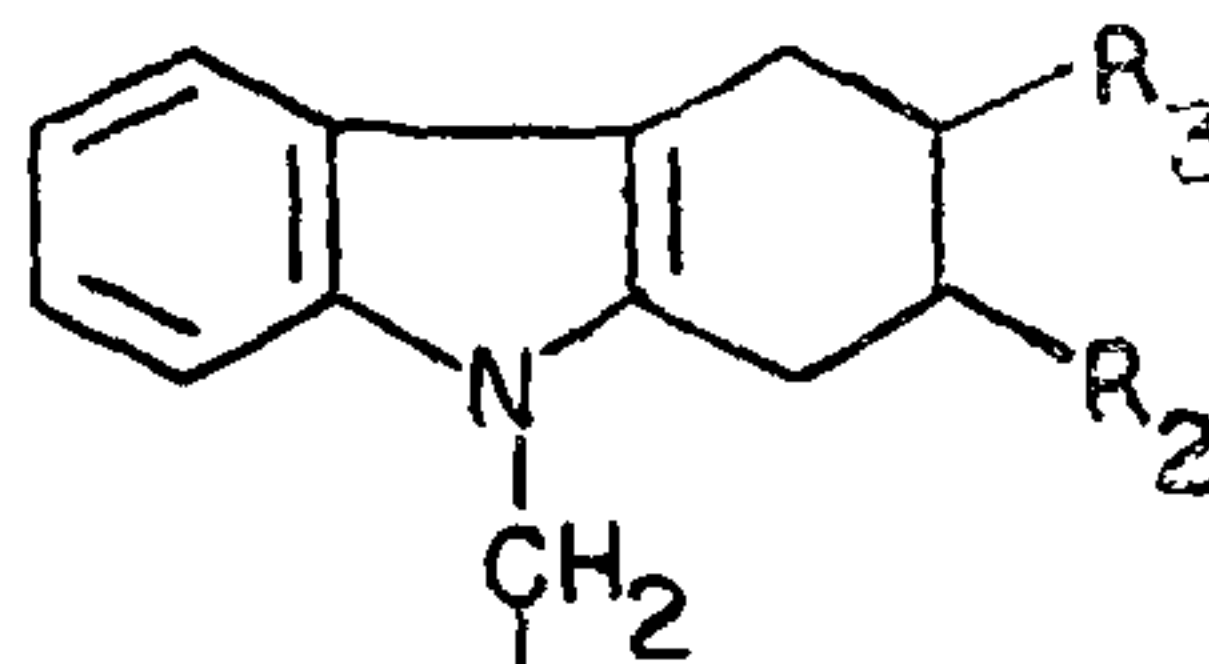
### SOME NEW BIS-TETRAHYDROCARBAZOLYL METHANE DERIVATIVES AND THEIR ANTIMICROBIAL PROPERTIES WITH RESPECT TO THOSE OF THE CORRESPONDING TETRAHYDROCARBAZOLES

PREVIOUS report reveals that the condensation of carbazole with formaldehyde takes place at 9-position rather than 3-position, if the 9-position remains unblocked<sup>1</sup>. On this ground we prepared three new bis-tetrahydrocarbazolyl methane derivatives (IV, V and VI) from the corresponding tetrahydrocarbazole derivatives (I, II and III)<sup>2</sup>.

Recent comparative studies of the pesticidal properties of some tetrahydrocarbazole derivatives along with carbazoles show that due to the presence of partially reduced moiety the pesticidal properties of tetrahydrocarbazoles are enhanced<sup>2</sup>. Now we report the studies of the antimicrobial properties of three new bis-tetrahydrocarbazolyl methane derivatives with those of the corresponding tetrahydrocarbazole derivatives,



- (I)  $R_2 = R_3 = \text{H}$   
(II)  $R_2 = \text{CH}_3, R_3 = \text{H}$   
(III)  $R_2 = \text{H}, R_3 = \text{CH}_3$



- (IV)  $R_2 = R_3 = \text{H}$   
(V)  $R_2 = \text{CH}_3, R_3 = \text{H}$   
(VI)  $R_2 = \text{H}, R_3 = \text{CH}_3$

The following procedure was adopted for the preparation of bis-tetrahydrocarbazolyl methane derivatives:

Paraformaldehyde was added to the acetic acid solution of the tetrahydrocarbazole derivative (I, II or III) and boiled for 2-3 minutes. After boiling small amount of 4% concentrated sulphuric acid in acetic acid was added when a precipitate was obtained. The product on crystallisation gave white crystals of bis-tetrahydrocarbazolyl methane derivative (IV, V or VI). Crystallising medium for bis-(9-(1,2,3,4-tetrahydrocarbazolyl)) methane (IV), m.p.  $145^\circ \text{C}$ , was cyclohexane, whereas bis-(9-2-methyl, 1,2,3,4-tetrahydrocarbazolyl)-methane (V), m.p.  $175^\circ \text{C}$ , and bis-(9-(3-methyl, 1,2,3,4-tetrahydrocarbazolyl)) methane (VI), m.p.  $165^\circ \text{C}$ , were crystallised from ethyl acetate and petroleum ether ( $40^\circ\text{--}60^\circ \text{C}$ ) mixture. Compounds (IV, V or VI) are soluble in cyclohexane, benzene, chloroform and ethyl acetate, but very slightly soluble in alcohol. Homogeneity of the compounds were studied by t.l.c.

Analytical data and IR spectral data are presented in Table I.

IR spectra of the compounds (IV, V and VI) show the absence of peak of  $-\text{NH}-$  group near about  $3400 \text{ cm}^{-1}$ , which was present in the spectra of the corresponding tetrahydrocarbazoles (I, II and III).