in portions over a period of 20 minutes. The mixture was then refluxed for 1 hour. Evaporation of the solvent dilution with water and extraction with ether gave a gum which recrystallised from acetone-ether to give (V), yield 900 mg (64·0%), m.p. 150–152° (lit.[6], m.p. 150–155°). The compound (V) was identical in all respects with an authentic sample (m.m.p. IR, NMR).

3-*Hydroxy*-9,10-*dimethoxyberbine* (*VI*)

The foregoing benzyl ether (V) (620 mg) was mixed with ethanolic-HCl (7·0 ml) and the mixture was refluxed for 8 hours. Ice pieces (5 g) were added to the cooled mixture and it was extracted with CHCl₃. The CHCl₃ layer was concentrated to give the crystals of (VI), m.p. 172° (acetone), yield 310 mg (63%). (VI) was identical in all respecss with an authentic sample (m.m.p. IR).

Department of Chemistry,   G. D. PANDEY.*
University of Allahabad,   K. P. TIWARI.**
Allahabad 211 002,
July 23, 1979.

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* For correspondence.

** Present address :   Hygiejnisk Institut, Dept. of Community Health and Environmental Medicine, Odense University, Odense C., Denmark.

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LEWIS ACID CHARACTER OF TETRAPHOSPHORUS TRISELENIDE (P_4Se_3)

THE ease of preparation of tetraphosphorus triselnide[1] has created some interest in its chemistry. As compared to tetraphosphorus tisulphide, very little is known about the nature of tetraphosphorus triselenide though it has a similar cage-like structure[2]. Penney and his coworkers[3] have reported a compound of iodine of composition $P_4Se_3I_2$ with it. No addition compound of bases with this molecule has been reported in literature. We report the isolation and characterisation of the adducts of organic tertiary bases with P_4Se_3.

Organic tertiary bases (B) such as pyridine, quinoline, α-picoline, piperidine, pyridine N-oxide give rise to P_4Se_3 . 2B while 1, 10-phenanthroline, N, N′-dioxide and 2, 2′-bipyridyl N, N′-dioxide form addition compounds of the composition P_4Se_3.B. Stoichiometric composition of these compounds has been established by elemental analysis which agrees with the calculated values within the limits of experimental errors. All these compounds are hygroscopic in nature. They change their colours and become liquids but are quite stable in dry air. They are insoluble in most of the polar organic solvents; therefore molecular weight and molar conductance values could not be determined.

Infrared spectra of these compounds especially in the low wave number region is very informative. The shift of electrons from nitrogen or oxygen of the base to the acceptor molecule results in the perturbation of their bands, identical to those observed in the complexes of these bases with metal halides[4] and acid halides[5,6] which are typical of the base coordination. The four principal bands between 1600–1430 cm⁻¹ due to C=C and C=N stretching vibrations are shifted to higher frequencies in the complexes, P_4Se_3 . $2C_5H_5N$ and P_4Se_3 . $2C_6H_7N$. Absorption frequency in the region 1230–1430 cm⁻¹ is considerably enhanced at 1388, 1328 and 1245 cm⁻¹. The strong band at 705 cm⁻¹ (the out of plane C-H deformation) and the band at 748 cm⁻¹ (the out of plane ring deformation), which are observed in the spectrum of pyridine, are shifted to 678 and 742 cm⁻¹ respectively in these complexes. The ring vibrations at 405 and 605 cm⁻¹ are shifted to 420 and 615 cm⁻¹. These shifts are characteristic of the coordination of pyridine through the nitrogen[4,7,8] which is supported by the formation of a new band at 500 cm⁻¹ assigned to Se–N stretching mode[9].

In the case of the compound P_4Se_3 . BipyO₂, the NO bending vibrations at 840 and 852 cm⁻¹ undergo a small negative shift due to the coordination on the NO group and the decrease in the double bond character[10]. The two NO stretching vibration in BipyO₂ shifts to lower frequency on coordination.

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[5,11]. Coordination of PhenO₂ to phosphorus atom of P₄Se₃ leads to the shift of ν(NO) 1269 and 1249 cm⁻¹ (bending) and δ(NO) 811 and 808 cm⁻¹ (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[12] 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⁻¹ in the case of pyridine adduct, at 412 and 398 cm⁻¹ in the case of pyridine N-oxide and in case of adducts of PhenO₂ and BipyO₂, these bands are observed at 420, 408 and 420, 412 cm⁻¹ 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⁻¹, not present in the parent compounds, suggests that phosphorus atom is the acceptor.

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Department of Chemistry,   K. C. MALHOTRA.
Himachal Pradesh University, J. M. BUTAIL.
Simla 171 005,   R. K. MAHAJAN.
*June* 18, 1979.   S. C. CHAUDHRY.

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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[1,2] as proceeding *via* two distinct steps obeying Michaelis-Menten kinetics.

$$Ce(IV) + Acetone \overset{K}{\rightleftharpoons} Complex$$

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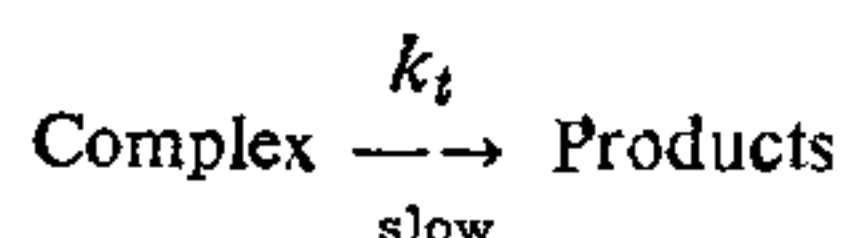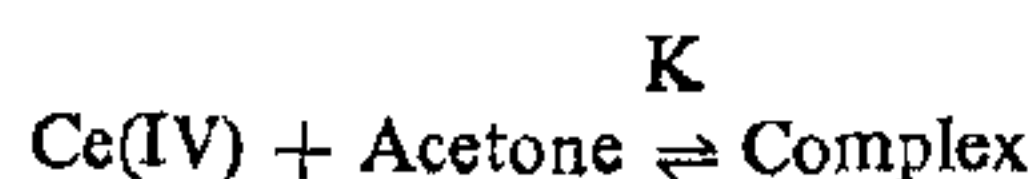
It is of interest to study the micellar-catalyzed reaction in order to find out whether the equilibrium constant K for complex formation or the rate constant k_t for the decomposition of the complex is affected since an increase in either K or k_t may lead to rate acceleration.

Experiments have been carried out under pseudo-first-order conditions with [acetone] $\gg$ [Ce(IV)], [Ce(IV)] = 3 – 4 × 10⁻⁴ mol. dm⁻³ [acetone] = 0·17 to 0·50 mol. dm⁻³, [HClO₄] = 1·0 mol. dm⁻³ and ionic strength, μ = 1·0 mol. dm⁻³ at 30° C. For the micellar-catalyzed reaction, the concentration of SDS is chosen as 1·35 × 10⁻³ mol. dm⁻³, one of the reported values[3] 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⁻¹ and k_ψ, s⁻¹ 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