of $\alpha$ is in close agreement with those of Zadkowski and Fleming[8] and Kosower and Kanety's[12] results who reported fluorescence lifetime to have little correlation with viscosity.

Kosower and Kanety[12] have reported that in 8,1-ANS, the radiative rate constant $(k_r)$ is mildly sensitive to solvent polarity and the variation in lifetime in solvents of different polarity is mainly due to intramolecular electron transfer from the charge transfer state. Such type of intramolecular electron transfer is recently proposed to be a barrierless process[21]. The activation energy calculated from the temperature-dependent studies is found to be 0.23 kcal/mol, indicating a very small barrier for the deactivation process and thus can be treated as a barrierless process.

The plot of fluorescence lifetimes against solvent polarity, $E_T$ (30), gives a straight line indicating that the fluorescence parameters in 8,1,-ANS are polarity-dependent (Figure 2). Summarizing, the deactivation process in 8,1-ANS has been found to be polarity-dependent whereas viscosity has rather insignificant effect indicating the absence of any large amplitude internal motion.

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# Preparation of octacalcium phosphate and its conversion to hydroxyapatite: An electron microscopic investigation

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Octacalcium phosphate has been prepared by a precipitation technique and characterized by X-ray, IR and electron microscopy. Its hydrolysis to hydroxyapatite has been investigated, the products are characterized by electron microscopy. A mechanism of hydrolysis is suggested.

OCTACALCIUM phosphate, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, OCP, is considered as a precursor in the formation of bones, teeth, renal stones, dental calculus etc.[1,2]

It has been synthesized earlier by the hydrolysis of Brushite[3], $\alpha$-tricalcium phosphate[4], and gel-diffusion method.[5] The precipitation of OCP at 60°C by Newsely[6] was found to be contaminated with hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, (HAP). We, therefore report here a new method of preparation of OCP under suitable conditions (temperature, 37°C and pH 7.2). Its formation is confirmed by X-ray, IR and electron microscopy. The mechanism of its conversion to hydroxyapatite has been proposed.

The chemicals used were AR (BDH or E. MERCK) grade. All solutions were prepared in $CO_2$-free double distilled water. A solution of calcium acetate, 9.9 mM/1 and another of ammonium dihydrogen phosphate, 5.9 mM/1 maintained at pH 7.2 were dropped simultaneously at a slow rate of 40 drops $min^{-1}$ to 400 ml of $CO_2$-free water taken in a flask maintained at 37°C. The precipitation was done at a constant ionic environment of 0.9 (Wt/Vol) NaCl and $CO_2$-free atmosphere. The precipitate was left in contact with the mother liquor at 37°C for 2 h to facilitate the ripening and homogeneity of the crystals. It was then washed with water, acetone and desiccated for seven days. The yield was about 60% of the theoretical. The crystals were flakey and lustrous white.

Calcium and phosphorus in the samples determined complexometrically gave Wt% CaO: 46.28 and $P_2O_5$: 43.03 and Ca/P g atom ratio 1.295. The number of water molecules was estimated by substracting CaO and $P_2O_5$ amounts from the total amount of sample weighed for analysis which corresponded to $5H_2O$ in the sample. The density of the sample was determined[7] to be 2.65 g cm$^{-3}$ (literature value[3] = 2.673 g cm$^{-3}$).

The X-ray diffractogram recorded using $CuK_\alpha$ radiation indicated that the sample obtained is Octacalcium phosphate[8]. The electron microscopic pattern of the sample obtained on a Simens Elmiskop is composed of blade-like habit (Figure 1a) and contained no extraneous phase confirming the purity of the sample. The

Figure 1. Electron microphotographs. *a*, (× 1200) *b*, *c* and *d*, (× 20,000).

IR spectra recorded on a Perkin Elmer grating spectrophotometer using KBr disc exhibited absorption bands at 1075, 1035, 910, 860, 599, 557, 525 cm$^{-1}$ and a broad band between 3650–3600 cm$^{-1}$ attributed to hydrogen bonded stretching modes of water of crystallization characteristic of OCP[9]. These results therefore indicate the suitability of the method for the preparation of OCP *in vitro*.

The conversion of OCP to HAP was studied by hydrolyzing the sample in the medium of precipitation under reflux. The samples after desired intervals of hydrolysis were centrifuged, washed, dried at 110°C and analysed complexometrically. The conversion of OCP to HAP was followed kinetically from the Ca/P g atom ratios of the products of hydrolysis. The different products are characterised by electron microscopy. The

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Table 1. Results of the products of hydrolysis of octacalcium phosphate.

| Time (min) | Wt% Ca | Wt% P | Ca/P g atom ratio |
|---|---|---|---|
| 0 | 33.06 | 19.14 | 1.30 |
| 10 | 36.07 | 20.92 | 1.32 |
| 20 | 38.05 | 19.14 | 1.49 |
| 30 | 37.57 | 17.67 | 1.61 |
| 90 | 38.57 | 17.67 | 1.63 |
| 150 | 38.57 | 17.67 | 1.63 |
| 240 | 38.85 | 17.67 | 1.65 |

results of hydrolysis of OCP is given in Table 1. The apatitic composition was attained after 30 min P(Ca/P = 1.60) which progressively increased to 1.65 at 4 h. Since the hydrolysis was done in the reaction medium containing a surplus of Ca ions in solution, the reaction taking place during hydrolysis can be represented as:

$$Ca_8H_2(PO_4)_6 5H_2O + 2Ca(OH)_2$$

$$\rightarrow 2Ca_5(PO_4)_3(OH) + 7H_2O$$
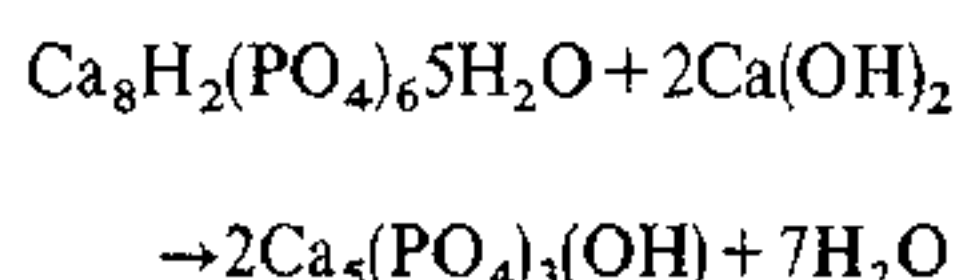
This is supported by the fact that *in vivo*, the tissue fluids contain a high concentration of calcium, which are essential for secretion of parathormone and continual osteoclastic resorption of bones. This calcium participates with the hydrolysis of OCP to hydroxyapatite of bone *in vivo*.

The electron micrographs in Figure 1, indicates the changes in the morphology of the crystals during different stages of hydrolysis. In the first stage of hydrolysis (Figure 1b), an interesting growth of hexagonal crystals of HAP are seen on the OCP structure. In Figure 1c, the host OCP contained more number of small crystallites of HAP. At the end of 4 h, distinct rod like crystals characteristic of crystalline HAP are seen in the micrograph (Figure 1d). This indicated the morphological changes of OCP from blade-like habit to rod-like habit of HAP after conversion. Since the lattice energy of a hexagonal structure of HAP is more than the weak structure of OCP, the formation of stable HAP crystal[10, 11] are thermodynamically favoured and the lattice of less stable OCP is ruptured along the faces about which the HAP crystals grow during hydrolysis.

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# Rose colouration of muscovite in rose mica schists from Manbazar–Gopalnagar, Puruliya district, West Bengal, Eastern India

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Rose coloured mica schists occur as small lensoid bodies in colourless mica schist of Manbazar-Gopalnagar areas. The rose colouration of these mica schists is imparted by muscovites which show distinct pleochroism in shades of rose colours. The rose colour of the muscovites is inferred to be due to their higher MnO content than the colourless muscovites.

THE precambrian rocks between Manbazar (23°4'N, 86°40'E) and Gopalnagar (23°8'N, 86°35.6'E), belonging to Chotanagpur terrain, Eastern India, are composed of a WNW–ESE running belt of mica schists with bands and lenses of amphibolites, greenschists (quartz–chlorite—epidote schists), quartzites, gondite and calc-silicate rocks. Rose mica schists occur in many localities (about 1.4 km north of Jitujori, 1.7 km SSE and 1.4 km south of Gopalnagar, 1.25 km north-east of Shyampur and 0.25 km south of Amakocha) as small patches and lenses, few metres to 20 m in length, within the dominant non-rose mica schists of usual silver grey or light colours[1]. The small quarry (20 × 10 m) to the south of Amakocha is composed dominantly of rose muscovite schists containing thin lenticular concordant patches of usual silver/grey muscovite schists. The intensity of rose colour of the rose muscovite schists varies from place to place in the same exposure, ultimately grading to usual silver/grey muscovite

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