been oxidised to the disulphide. The presence of polymeric products in the present study would also suggest the formation of thiophenol[4].

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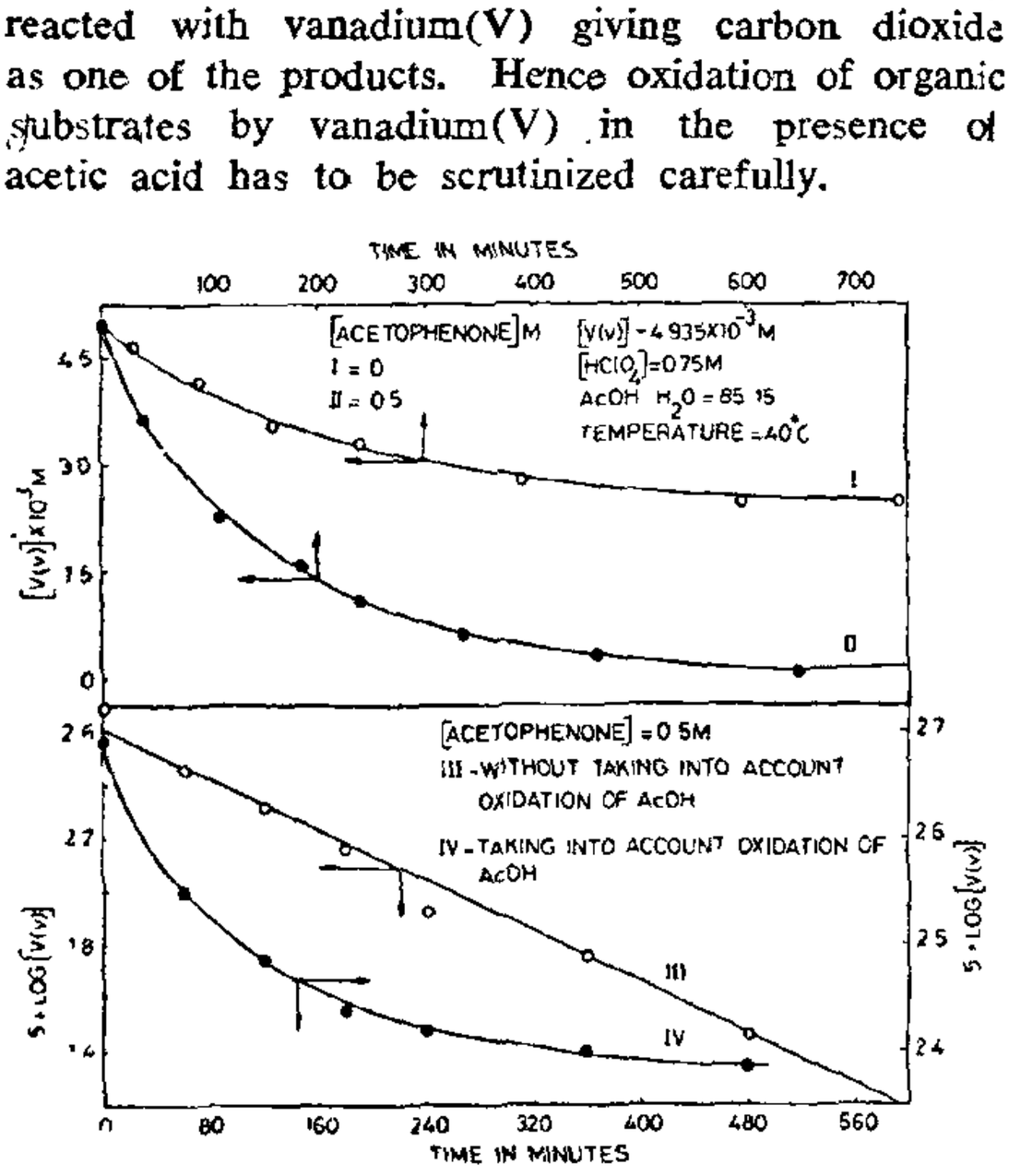
ON THE OXIDATION OF ACETOPHENONE BY VANADIUM(V) IN AQUEOUS ACETIC ACID

A SEARCH of the literature on the oxidation of organic substrates using vanadium(V) shows that many such oxidations are carried out in the presence of acetic acid[1-4]. Our investigations show that acetic acid purified by the procedure suggested by Orton and Bradfield[5] (freezing point 16·6° C) reacted with vanadium(V) giving carbon dioxide as one of the products. Hence oxidation of organic substrates by vanadium(V) in the presence of acetic acid has to be scrutinized carefully.



CONCENTRATION-TIME CURVES AND FIRST ORDER PLOTS FOR VANADIUM(V)

FIG. 1

Misra *et al.*[6] have reported a good first order, with respect to vanadium(V) for the oxidation of acetophenone by vanadium(V) in 85% acetic acid. They have not considered the possibility of a reaction of vanadium(V) with the medium. We have observed that in the oxidation of acetophenone by vanadium(V) ($4{\cdot}95 \times 10^{-3}$ M) in 85% acetic acid about 50% of the vanadium(V) was used up in the reaction with the solvent itself.

Since the reaction of the solvent can be followed independently, it is possible to separate the oxidation of acetophenone from the reaction with the solvent when both reactions are taking place simultaneously. If we ignore the reaction of the solvent with vanadium(V) a neat first order with respect to vanadium(V) is obtained. If we consider the reaction with the solvent also, the results do not fit into a first order plot (Fig. 1).

The intermediates formed in the reaction with the solvent may interfere with the oxidation of the substrate, making the study of the substrate oxidation in presence of acetic acid complex. Further work is in progress to understand the reaction of vanadium(V) with acetic acid.

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DIGESTIVE ENZYMES OF PANCREAS IN NORMAL AND THIAMINE DEFICIENT RATS

ANOREXIA is one of the prominent symptoms associated with thiamine deficiency[1-3]. Whether it is due to a defect in the production and secretion of digestive enzymes is not clear. In the present communication the amylase, lipase and proteolytic activities of pancreas of normal and thiamine deficient rats have been determined and reported.

Thiamine deficient male albino rats[4] along with their normal controls were sacrificed in the fed state, pancreatic tissue cut out, weighed quickly and homogenized in saline or buffer using Potter-Elvehjem homogenizer chilled in ice. For proteolytic activity, the homogenization was carried out in 0·01 M tris (hydroxymethyl aminomethane)–0·03 M $CaCl_2$

buffer pH 7·5 for 5 min. at 0–4° C and the extent of digestion of casein in 30 min. at 37° C and pH 7·5 was estimated by the method of Kunitz[5]. Enterokinase was added to the homogenate and incubated for 1 hr for activation of the zymogen, before the addition of casein substrate. The reaction was stopped by addition of 10% trichloracetic acid and the tyrosine liberated estimated in the filtrate. The proteolytic activity is expressed as μ moles of tyrosine liberated/hr.

For amylase activity, the tissue was homogenized in 0·01 M KH_2PO_4–0·85% (w/v) NaCl buffer pH 6·5 and centrifuged at 10,000 g at 0° C in a MSE Mitral 2L refrigerated centrifuge and the supernatant fraction used. The digestion of starch at 37° C was measured as maltose after incubation forr 10 min. and precipitation by 0·3 N $Ba(OH)_2$ and 5% $ZnSO_4$ using the methods of Somogyi[6] and Nelson[7]. The amylase activity is expressed as that amount of enzyme which librates 1 mg of maltose/10 min.

Lipase activity was determined by using homogenates in 0·85% (w/v) NaCl by the method of Clarke[8] using olive oil-bile-glycerol mixture in 0·05 M NH_4Cl—ammonia buffer pH 8·0 containing $CaCl_2$. The lipase activity is expressed as ml of N/20 KOH required for tritration of fatty acids liberated/4 hr.

The nitrogen content was estimated by the micro-kjeldahl method[9].

When expressed per g fresh weight of pancreas or per mg tissue nitrogen, both amylase and proteolytic activities were elevated ($p < 0·01$ and $< 0·02$) in thiamine deficient pancreas, while lipase activity appeared unaffected. However, when the enzyme activity of the whole pancreas was considered, the lipase activity was decreased to 1/3 of the value for normal ($p < 0·001$) (Table I).

TABLE I

Digestive enzymes of pancreatic tissue of normal and thiamine deficient rats

	Group	Weight of pancreas	Amylase activity	Proteolytic activity	Lipase activity
Per g fresh weight of tissue	Normal	0·454±0·067*	5483±1108	62± 6	400±33
	Thiamine deficient	0·155±0·010	16983±3389	253±69	414±61
	p value	$< 0·01$	$< 0·01$	$< 0·02$	N.S.
Per mg tissue nitrogen	Normal	..	221± 39	2·5± 0·2	16·1± 1·3
	Thiamine deficient	..	499± 96	7·8± 2·1	13·3± 2·0
	p value	..	$< 0·01$	$< 0·02$	N.S.
Per whole pancreas	Normal	..	2490±503	28·5± 3·02	182±15·2
	Thiamine deficient	..	2632±525	39·3±10·82	64± 9·5
	p value	..	N.S.	N.S.	$< 0·001$

* Standard Error. N.S.— Not Significant.

The results show that the amylase and proteolytic enzymes are not decreased in proportion to decrease in pancreatic weight or nitrogen content. The lipase on the other hand is decreased under these conditions and thus shows no change in specific activity. The study, therefore, does not indicate whether thiamine is directly involved in maintaining the enzymes of exocrine pancreas and further work is needed to explain the reason for the anorexia in thiamine deficiency.

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BIOGENIC PROTODOLOMITE FROM THE LIMESTONES OF BOMBAY HIGH OIL FIELD

DURING the course of petrographic investigation of the limestones from the subsurface of Bombay High offshore oil field, small unit rhombohedra of the average size of 6 to 7 microns were noticed forming constituent particles of the micritic base of many micritic limestones. The grains are euhedral, water-clear, somewhat wine yellow in colour and devoid of any inclusions. The accompaying photomicrograph (Fig. 1) shows the morphology and mode of occurrence of the unit rhombohedra as a part of micritic base of the micritic limestones.

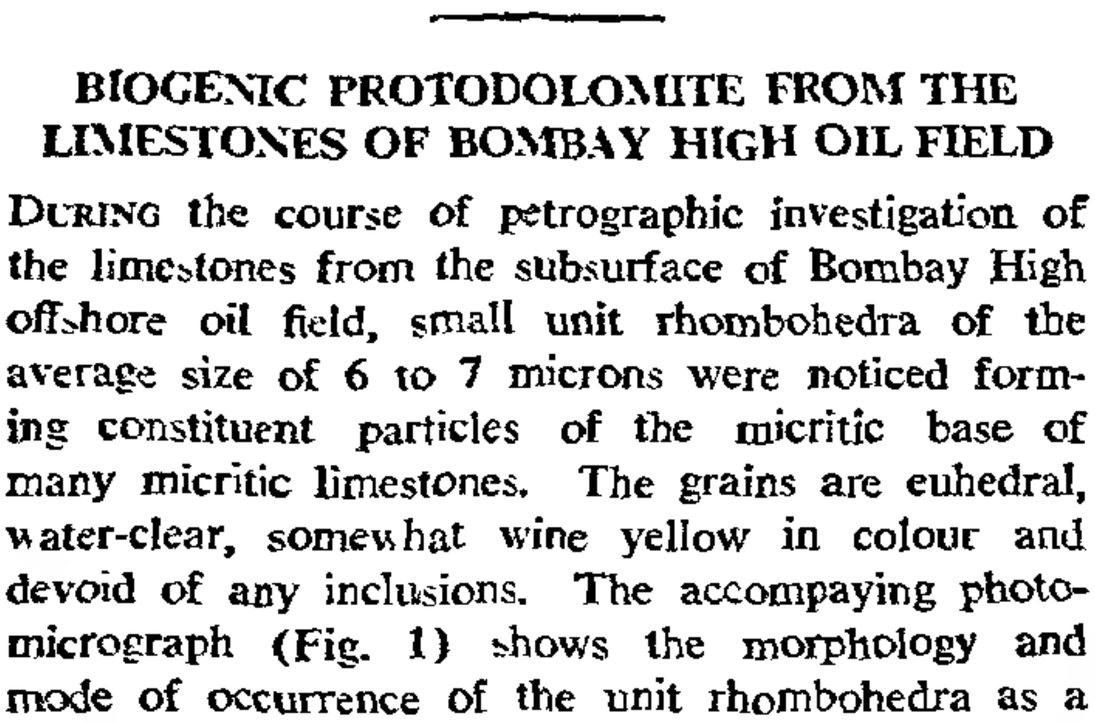

FIG. 1. Thin section of micritic limestone from a core sample of Bombay Offshore oil field showing protodolomite unit rhombohedra, × 400.

Figure 2 is an X-ray trace of a powder mount of a rock sample containing the unit rhombohedra. There is a prominent peak for calcite (3·04 Å *d*) and a peak in the range 2·93 Å *d* to 2·95 Å *d* spacings. On several X-ray traces of the same mount taken at different places and on mounts of other samples containing unit rhombohedra, the 2·93 Å peak was seen to shift its position down to 2·90 Å *d*. The $MgCO_3$ content in the mineral as read from Goldsmith *et al.* chart (1955)[2] is from 26 to 40 mol per cent in calcite. Dolomites reported from sedimentary rocks (Goldsmith and Graf, 1958) and from many modern hypersaline lakes (Bathurst, 1971)[1] contain about 5 mole per cent excess calcium than the requirement of a 1 : 1 stoichiometric dolomite (2·88 Å *d*) and therefore called by them as protodolomite. The nearest approach the mineral under study is the biogenic protodolomite reported by Schroeder *et al.* (1969)[5] from the tooth of a living echinoid. Due to lack of a better term, the mineral under report is also regarded as a protodolomite.

FIG. 2. X-ray chart at 20 2θ rotation per minute showing the peak position of calcite and protodolmite of the sample depicted in the micrograph.

Many invertibrate and plant marine organisms are composed of Mg calcites. Many algae and echinoderms contain Mg calcites in their skeletal architecture. Calcareous algae contain more than 20% Mg in their calcite and echinoderms about 40% (Millman, 1974)[4]. Besides, many skeletal parts of echinoderms contain different concentrations of Mg. Smaller spines contain larger amounts (Millman, 1974). In this connection it is interesting to note that in the thin sections of Bombay rocks, containing a large micrite base and abundant unit rhombohedra, there are very fine comminuted echinoderm skeletal fragments and many show grain diminution to minute unit rhombohedra. Millman (1974)[4] writes: "Many marine organisms precipitate magnesian calcite. During diagenesis the magnesium may be liberated and thus form magnesium rich interstitial waters which may be subsequently precipitated as dolomite." Such a process may be envisaged for Bombay High rocks also. For the