

STUDIES ON CHEMICAL EVOLUTION OF TRANSITION METAL ENZYMES

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Taking early biological conditions into account, Egami (1974) proposed that chemical evolution and origin of life took place in primeval seas. The most abundant transition elements in primeval sea were iron, zinc, and molybdenum (50-100nM) which are also found as essential components of many enzymes. It is further proposed that enzymes containing these metals are responsible catalyzing vital reactions necessary for life processes. Investigations are carried out by us as an attempt to explore evolutionary paths of metalloenzymes. The underlying assumptions are those of Egami (1975), Calvin (1959), and Beck (1978). Considering the significance of amino acid mixed ligand cyano complexes of iron and amino acid complexes of zinc, the work was undertaken by synthesizing complexes of the type

$[\text{Fe}(\text{CN})_5(\text{L})]^{n-}$ and $[\text{Zn}(\text{L})]^{n-}$ where L=amino acids or peptides. The catalytic activity of these complexes was studied in reactions of potential evolutionary significance. The following conclusions are drawn as a consequence of experimental observations:

1. The complexes of the type $[\text{Fe}(\text{II})(\text{CN})_5(\text{L})]^{n-}$ are found to be fairly efficient catalysts for the decomposition of H_2O_2 (Kamaluddin et al., 1986; 1988). The catalytic activities of these complexes were increased when ligand L is subsequently substituted by glycine, histidine, imidazole, and triglycine. Furthermore, catalytic activities depend on the formation of active intermediates, $[\text{Fe}(\text{CN})_5(\text{OH}\dots\text{OOH})]^{n-}$.

Decomposition of hydrogen peroxide catalyzed by $[\text{Fe}(\text{CN})_5(\text{L})]^{n-}$ complexes conform to Michaelis-Menten type kinetics.

2. Redox reactions like the dehydrogenation of ascorbic acid and NADH when coupled with reduction of methylene blue are also catalyzed by $[\text{Fe}(\text{II})(\text{CN})_5(\text{L})]^{n-}$ complexes. Tentative mechanisms for the dehydrogenation reactions have been proposed and the related rate law has also been established (Kamaluddin et al., 1989).

It is believed that on the primitive earth when reducing potential of the atmosphere was not high enough, the lower oxidation state iron complexes like $[\text{Fe}(\text{II})(\text{CN})_5(\text{L})]^{n-}$ might have been involved in dehydrogenation type of activity.

3. Experimental observations mentioned above revealed that the mixed ligand cyano complexes of iron are able to catalyze a class of redox

reactions like the decomposition of H_2O_2 and dehydrogenation of ascorbic acid and NADH. It can therefore be considered that formation of such complexes might have been an important stage where replacement of primary ligands by biologically important molecules increase the catalytic activity of metal complexes in the course of evolution of metal containing enzymes.

4. Zinc amino acid complexes, which closely resemble enzymic coordination sites of zinc metalloenzymes are able to catalyze hydrolysis of p-nitrophenylacetate and p-nitrophenyl phosphate. The catalytic activities of complexes were found to be maximum if the binding sites are available to substrates.

It is postulated that evolution of zinc containing enzymes might have proceeded via formation of zinc amino acid complexes of peptides and proteins with histidine residues at coordination sites.

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