

THE ACID-ALKALINE TRASITION OF A SEA TURTLE MYOGLOBIN

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The microenvironment of the iron in a sea turtle myoglobin "Dermochelys Coriacea" (MbT) is studied using the spectroscopic techniques EPR and optical absorption. Optical absorption spectra in the visible region suggests a great homology between MbT and other myoglobins like whale, human and elephant. The pK of the acid-alkaline transition is 8.4 slightly lower than the pK of whale and equal to that of elephant myoglobin. The EPR measurements of the iron spectra are consistent with a change in heme pocket hydrophobicity and in the charge distribution in the distal region. The spectrum at pH 7.0 is characteristic of a high spin configuration with axial symmetry ($g_x = g_y = 5.95$). At higher pH this signal changes in a way different from that observed for whale myoglobin. We observe for MbT both the formation of a low spin configuration with rhombic distortion ($g_x = 2.56$, $g_y = 2.20$, $g_z = 1.90$) and of a high spin species with rhombic distortion ($g_x = 6.79$, $g_y = 5.18$, $g_z = 2.12$). This suggests a lowering of symmetry at the heme so that now the x and y directions are no more equivalent. This can be explained by amino acid substitution at the distal positions of heme or to off axial positioning of distal residues. The coexistence at high pH (pH = 11.0) of these two spin forms could be explained by the existence of two protein conformations where the crystal field splitting factor Δ and the electron exchange energy are of the same order allowing the presence of different configurations simultaneously. The presence of different kinds of hemes is ruled out by the experiments with nitrosyl MbT-F showing spectra very similar to those of whale myoglobin. The pK of the acid-alkaline transition 8.3 obtained from EPR spectra agrees very well with results from optical absorption.

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A HIGHER REACTIVITY OF IMIDAZOLE GROUP IN N^α-BENZOYL-SUBSTITUTED-HISTIDINES TOWARDS p-NITROPHENYL ACETATE

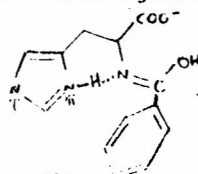
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The reactivity of imidazole group towards p-nitrophenylacetate (PNPA) was studied with several imidazole containing compounds and a Bronsted relationship has been determined between the second order rate constants (k_2) for the reaction and the pK_a of amidazole groups: $\log k_2 = 0.569 \text{ pK}_a - 2.755$ (Juliano et al. *Biorganic Chemistry* 11, 383, 1982). N^α-benzoyl histidine and N^α-benzoyl histidine methyl ester have k_2 values 2 - 3 times higher than expected by the above Bronted relationship. The reactions with these two compounds with PNPA followed a second order rate process and the k_2 values are independent of pH. These higher values for k_2 are dependent on the benzoyl group be bonded directly to N^α-amino group of histidine.

The N^T is the only nitrogen of the imidazole group in histidines that is reactive towards PNPA, and the tautomeric ratio N^T-H/N^N-H is around 4. Therefore, any decrease in this ratio will make N^T more available, increasing consequently the imidazole group reactivity. A hydrogen bond, as shown in the scheme below, could favour the N^N-H tautomer, decreasing the above mentioned tautomeric ratio. Furthermore, this hydrogen bond is possible only with the phenyl group attached to carbonyl group of amide bond. This hypotesis is under investigation in our laboratory.

Scheme



N^α-Benzoyl-histidine in iminol form

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