CHEMICAL SIMILARITIES OF DI-OXA[15]ANNULENONE CYCLE WITH BACTERIORHODOPSIN CYCLE

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Chemical similarities between the titled cycles were investigated in the following three points.

1. Equilibria of four chemical species in the [15]annulenone cycle (Fig. 1a) were studied as function of variable proton concentrations. It was shown that (i) the entire equilibria of TH^+, CH^+, T and C can be described by K_{a_t}, K_{a_c}, and α; and that (ii) unequal proton binding occurs as a consequence of photoisomerization $TH^+ \rightleftharpoons CH^+$, only when following inequalities are satisfied; $pK_{a_c} > pK_{a_t}$ and $\alpha < 1$. ^{1}H-NMR experiments conducted in CD_2Cl_2 FSO_3H suggested that these requirements hold for TH^+ and CH^+ species.

2. Mechanism of photoisomerization $TH^+ \rightleftharpoons CH^+$ We obtained a strong experimental support which shows that the photoisomerization involves "Förster Mechanism". The pK_a^* of TH^+ in excited state was obtained as ca. -5.5, whereas the pK_a of the same species at -60°C was + 5.2 in CD_2Cl_2.

3. Thermal relaxation rates of the photoproducts The rates and temperature effects of thermal back-isomerization of photoproducts [$CH^+ \rightarrow TH^+$ in the annulenone cycle, and $M_{412} \rightarrow B_{568}$ in bacteriorhodopsin cycle (Fig. 1b)] were compared. These comparisons indicated that (i) rates are almost comparable in both cycles, and that (ii) methyl group introduction causes similar rate accelerations when compared with those of the corresponding desmethyl derivatives [R = H in stead of Me in Fig. 1b and 1a].

Above results obtained led us to convince that the [15]annulenone cycle is mimic to bacteriorhodopsin cycle in its chemical transformations, in equilibria, and also in photoisomerizaton mechanism.

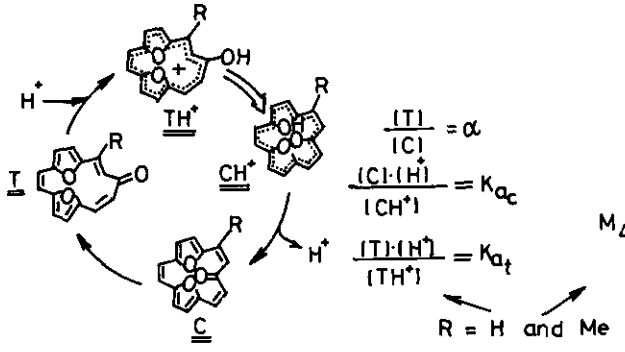

Fig. 1a

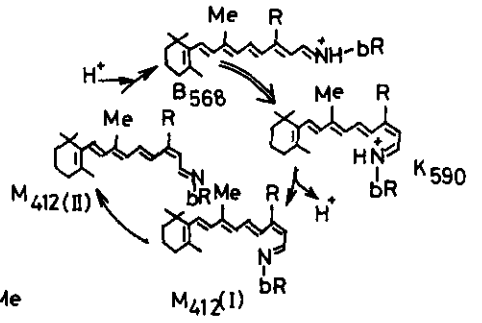

Fig. 1b