Title:	Bio/Nano-catalytic proton transfer
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Abstract:	We have studied the catalytic property of different biomolecules, nanoparticles and nucleotides towards Kemp Elimination, a proton transfer reaction. The chosen substrate is 5- nitrobenzisoxazole, which gave the ring opening product, 2-cyano-4-nitrophenol under catalytic conditions. The biomolecule, cytochrome c is one of the most primitive and omnipresent protein and it is known that enzymes and proteins formed in the early days of the evolutionary cycle possess greater enzyme promiscuity i.e. has greater substrate specificity to catalyze multiple reactions, compared to the lately evolved ones. We have investigated and found that cyt c, whose primary function is in electron transfer during respiratory process, shows enzyme promiscuity towards Kemp Elimination reaction in presence of membrane- mimetic media like micelles and vesicles. We have already shown that cytochrome c unfolds upon binding to vesicular or micellar membrane and exposes its heme moiety, wherein the Fe 3+ center binds the substrate and proximal histidine acts as the base. We further did mutation experiments, wherein we replaced the His-18 residue with Alanine and found that the catalytic rate drastically reduced. This solidified the fact that the proximal His-18 residue of cyt c actually acts as the base to catalyze the reaction via a base-promoted E2 elimination. We also studied the competition between redox-mediated and base-mediated mechanisms of catalysis in presence of oxidizing and reducing agents, at different pH. We have also investigated the effect of different organic solvents and inorganic salts on the rate of KE, both in bulk and in nanoconfined environment (i.e. inside the hydrophilic core of reverse micelles). We further extended this work and found that CTAB-capped gold nanoparticles and gold nanorods also showed high catalytic activity towards KE, in comparison to simple CTAB micelles. As a result of the formation of negatively charged TS on positively charged GNR surface, surface charge altered and led to the self-assembly of GNR during the reaction. This enhanced diffusion of GNR only during catalytic conversion can also be a contributing factor. The catalysis rate and extent of assembly formation is depended on the pH of the system. The clustered nanorods has been used as a nanoreactor to 8catalyze a second reaction (via S N Ar mechanism), which is completely independent of our primary reaction (KE). Lastly, we have also examined the effect of different adenine nucleotides (ATP, ADP, AMP) in presence of GNP system and found that the catalytic power is depended on the local surface pH of the GNP, which is further depended on the extent of multivalent interaction between the nucleotides and the GNP. The GNP surface changes from acidic to basic on changing the nucleotide from ATP to AMP. We have also shown this change in-situ by using the enzyme, Potato Apyrase, which can cleave ATP to AMP and thus enhance the KE activity, resulting in catalytic upregulation in a temporal manner. Thus, such kind of study helps scientists to understand the surface chemistry of nanoparticles, how catalytically driven enhanced diffusion and self-assembly of nanorods occur and also to design nanomaterials with emergent, innovative and cascading catalytic properties. It also helps scientists to understand natural processes, like flocking of birds or bacterial colonization, which are necessary functions for their sustainability and natural catalytic systems that can tune their catalytic performance in response to external factors like pH, better, so that synthetic systems with nature mimicking properties can be developed.
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