Mechanistic Insights into HCO$_2$H Dehydrogenation and CO$_2$ Hydrogenation Catalyzed by Ir(Cp*) Containing Tetrahydroxy Bipyrimidine Ligand: The Role of Sodium and Proton Shuttle

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The mechanism of HCO$_2$H dehydrogenation catalyzed by [IrCp*(H$_2$O)(bpymO$_4$H$_4$)]$^{2+}$, (bpymO$_4$H$_4$ = 2,2′,6,6′-tetrahydroxy-4,4′-bipyrimidine) was investigated using density functional theory. The relative free energy profiles at various protonation states, corrected to pH 3.5 and pH 7.6, suggested that Na$^+$ together with the ortho-oxyanion of bipyrimidine facilitates the formation of the Ir-HCO$_2$, subsequent hydride transfer, and H$_2$ formation. HCO$_2$H was found to be a more effective proton shuttle than H$_2$O for H$_2$ formation. Under experimental conditions, the highest catalytic reactivity was found at pH 3.5-4.0, where both HCO$_2$Na and HCO$_2$H are present. At lower pH, at low formate concentration, HCO$_2$H dehydrogenation tends to proceed via a Na$^+$ independent pathway, involving a higher energy barrier. At higher pH, although Na$^+$ can mediate hydride transfer and H$_2$ formation, the low amount of HCO$_2$H results in H$_2$O as the proton shuttle, which involves a higher energy barrier than HCO$_2$H proton shuttle. That is, the catalytic activity of HCO$_2$H dehydrogenation by the proton-responsive Ir complexes at different pH values is influenced by the protonation state, involvement of Na$^+$, and the availability of HCO$_2$H as a proton shuttle. For the hydrogenation of CO$_2$ at pH 8.3, the rate determining step is heterolytic cleavage of H$_2$ mediated by Na$^+$, via a HCO$_3^-$ proton shuttle. Our results demonstrate the importance of alkali metal ions in the design of catalysts for efficient, reversible, CO$_2$ conversion.