Computational Chemistry of Vanadate Complexes with Biogenic Ligands: Structure, Properties, and Reactivities.

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Complexes of vanadate(V) and peroxovanadate(V) with glycyclglycine, the simplest dipeptide, and imidazole, a model for histidine, are studied at appropriate levels of density functional theory. Special attention is called to effects of thermal motion and the solvent, water, on structures and ^{51}V NMR chemical shifts by explicitly following the short-time dynamics of the aqueous solutions[1] using Car-Parrinello molecular dynamics (CPMD) simulations. For the vanadate-dipeptide complex **1**,[2] the simulations rapidly converge to a five-coordinate, anionic species (Fig. 1), which is suggested to be the major constituent of the actual solution at pH 7.

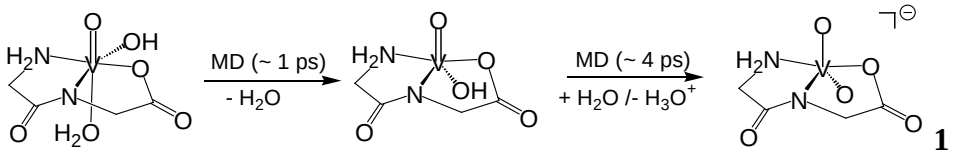

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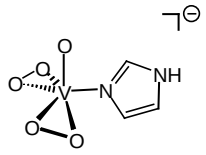
Figure 1: Structural changes of glycyclglycine-vanadate during a CPMD simulation in water.



For peroxovanadate complex **2**, a structural model for vanadium-dependent haloperoxidases, the simulations predict a significant reinforcement of the vanadium-imidazole bond upon going from the gas phase into solution.[3] For olefin epoxidation, a typical O-transfer reaction catalyzed by such complexes, the oxygen transfer from **2** to the substrate is identified as the rate-limiting step in the catalytic cycle (using H_2O_2 as oxidant). The corresponding barrier is substantially reduced by adding a H-bond acceptor to the imidazole ligand. Implications for the enzymatic mechanism and requirements for prospective biomimetic analogs are discussed.

References

(1) M. Bühl, M. Parrinello, *Chem. Eur. J.* **2001**, *7*, 4487.
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(3) M. Bühl, R. Schurhammer, P. Imhof, *J. Am. Chem. Soc*. **2004**, *126*, 3310.