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THEORETICAL INSIGHTS INTO THE HALOPEROXIDASE MECHANISM OF VANADIUM COMPOUNDS

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Vanadium compounds are of significant interest in biochemistry, mainly acting as catalysts for the mild halogenation of organic molecules, akin to haloperoxidase enzymes[1]. The mechanisms of this catalysis vary among different vanadium compounds[2,3]. Aiming to elucidate the catalytic activity of $[HV^{V}O(O_2)_2(bipy)]\cdot 3H_2O$ (**C**) in the bromination of organic molecules, theoretical studies were conducted to propose a reaction mechanism that explains the formation of HBrO – the responsible for the halogenation process. Density functional theory (DFT) calculations were performed and the transition states were identified by their single imaginary vibrational mode after frequency analysis, and they were further validated using the Intrinsic Reaction Coordinate (IRC). In Figure 1, calculated mechanisms delineate three pathways (I, II, III) converging at the same intermediate (i-1), associated with hypobromous acid formation, which subsequently reacts with oxygen peroxide to regenerate the pre-catalyst **C**. All pathways are exergonic with ΔG values of -5.25, -9.21, and -16.63 kcal mol^{-1}, sharing the same activation energy (19.77 kcal mol^{-1}) between i-1 and TS1. These findings align well with expected barriers for analogous reactions involving diverse vanadium compounds, demonstrating the feasibility of these catalysts for halogenating organic molecules under mild conditions. The presented results are significant as they shed light the details of the reaction mechanism studied, potentially guiding the tailored synthesis of new catalysts with enhanced performance.

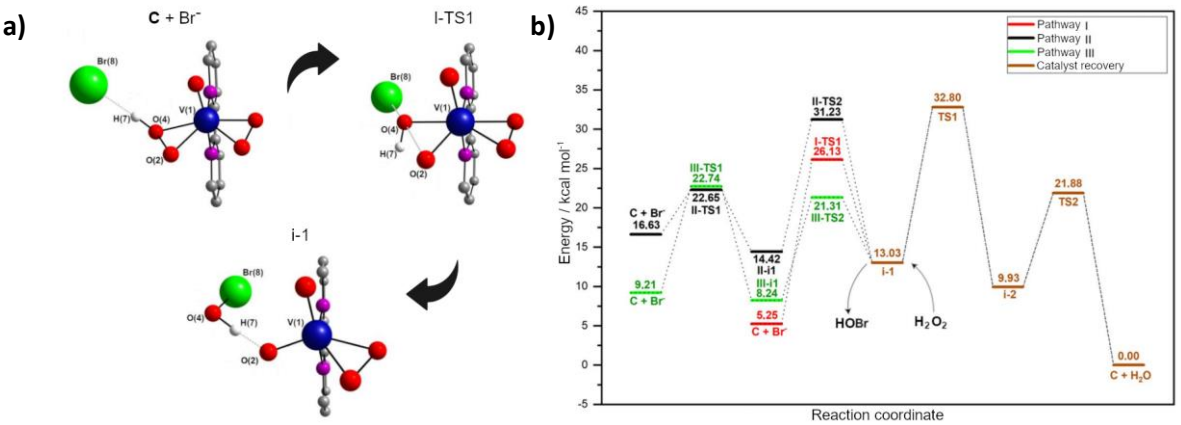

Figure 1: **a**) Example of Pathway I for the formation of HOBr from the reaction of C with Br^- **b**) Free energy profile for the reaction pathways calculated for the formation of HOBr using **C** as a catalyst.

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