

Mechanism of the Reductive Activation of O₂ to O₂²⁻ from a Vanadium(IV) Species and Its Potential Use in Fuel Cells

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The two electron reductive activation of O₂ to O₂²⁻ is of particular interest to scientific community mainly due to the use of peroxides as green oxidants and in powerful fuel-cells. Among the metal-ions which activate O₂, vanadium is of particular interest because of its numerous oxidative catalytic properties. Reaction of either V^{IV}OSO₄·3.5H₂O or V^{IV}OCl₂ with [N-\(8-quinolyl\)pyridine-2-carboxamide](#) (Hpbq) in CH₃OH solution under atmospheric O₂, at room temperature, resulted in the quick formation of [V^{VO}(k²-O₂)(pbq)(H₂O)](1). Compound 1 constitutes a rare example of formation of a (peroxo)oxidovanadium(V) complex from molecular O₂ and an oxidovanadium(IV) complex. The reaction of formation of compound 1 vs. time was monitored by ⁵¹V and ¹H NMR, UV-vis, cw-X-EPR, Resonance Raman spectroscopies and cyclic voltammetry revealing the formation of a stable radical intermediate [V^{VO}(k²-O₂)(pbq)(H₂O)]^{•+}. Dynamic experiments in combination with computational calculations were used to elucidate the mechanism of the reaction. The galvanic cell {Zn|V^{III},V^{II}||cis-[V^{VO}O₂(bpq)], [V^{VO}(O₂)(bpq)(H₂O)], [V^{IV}O(bpq)(H₂O)₂]⁺|O₂|C(s)} was manufactured, demonstrating that this technology can be used in Zn|H₂O₂ fuel cells generating H₂O₂ *in situ* from atmospheric O₂.