OXIDATION CATALYSIS BY POLYOXOMETALATES: FUNDAMENTAL ELECTRON-TRANSFER PHENOMENA

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Early transition-metal oxygen-anion clusters (polyoxometalates, POMs) are a large and rapidly growing class of versatile and tunable oxidation catalysts. All key molecular properties of these clusters (composition, size, shape, charge density, reduction potential, solubility, etc.) can be systematically altered, and the clusters themselves can serve as tunable ligands for controlling the reactivity of a wide variety of transition-metal cations. As a result, POMs catalyze reactions of a vast array of inorganic or organic oxidants [1]-[3]. Electron-transfer, including outer-sphere processes, is central to all these reactions. Despite decades of study, however, there is little consensus regarding fundamental parameters pertinent to application of theoretical models of outer-sphere reactions, such as those of Marcus, Sutin and others [4]. Keggin anions (general formula $[X^nW_{12}O_{40}]^{(8-n)-}$), which are effectively spherical (T_d symmetry) small (r = 5.6 Å) are excellent candidates for obtaining the information needed to address these outstanding fundamental issues.

In this work, we present such information. It was acquired using a series of Keggin anions (heteroatoms X = Al(III), Si(IV), P(V), and select derivatives) specifically chosen or designed for this purpose. Surprisingly, the reorganization energy associated with electron-transfer reactions involving POMs with aluminum as the heteroatom (X = Al(III)) were remarkably larger than could be accounted for by the systematic change in charge density imposed by varying X from P(V) to Si(IV) to Al(III) [5]. To understand this finding in the context of the assumptions and parameters associated with Marcus theory, additional kinetic data were obtained. Reactions studied included cross reactions between POMs possessing similar yet systematically varied structures and between select POMs and a theoretically well-characterized $Fe(CN)_6^{3-}$ probe. These data provide insight into the unexpectedly small rate constant (hence, large reorganization energy) observed for electron-transfer involving anions with the Al(III)-heteroatom.

These data and insights were then applied to analysis of rate constants observed for one-electron transfer from a reduced Al(III)-containing POM to dioxygen. The experimental rate constant observed for this key, and here rate-limiting, step in POM-catalyzed reactions of dioxygen was close to theoretical. Also addressed by these data is the effect of localization of redox-active sites within the POM cluster on outer-sphere reaction rates.

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