Control of Electron Transfer for Efficient Oxygenation Reactions

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Electron transfer is the most fundamental reaction to govern chemical reactions. To find an effective way to control electron transfer, transient active species were prepared at low temperature under inert atmosphere. Electronic structures of these active species were investigated with various techniques including absorption, ^{1}H and ^{2}H NMR, EPR, IR resonance Raman spectroscopy and magnetic susceptibility measurement. Correlations between electronic structures and electron transfer ability are investigated in detail.

1. Dioxygen Activation via Two-Electron Transfer from Hydroxide to Dioxygen Mediated By a Manganese(III) Complex

Although atmospheric dioxygen is regarded as the most ideal oxidant, O_2 activation for use in oxygenation reactions intrinsically requires a costly sacrificial reductant. This study investigated the use of inexpensive aqueous alkaline solution for O_2 activation. This study has clarified that a manganese (III) salen complex mediates O_2 activation in the presence of OH^- from 2 M KOH aqueous solution (Figure 1). Mechanistic investigation have shown that the reaction of Mn^{III}(salen)(Cl) with OH^- generates a transient species with strong reducing ability, which effects the reduction of O_2 by means of a manganese(II) intermediate.

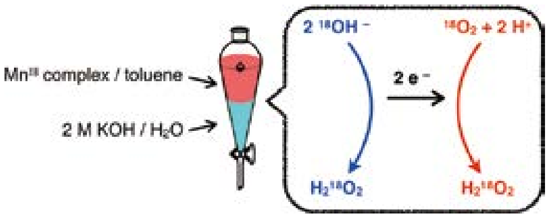

Figure 1. Isotope experiments to verify two-electron transfer from OH^- to O_2.