

# 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,  $^1\text{H}$  and  $^2\text{H}$  NMR, EPR, IR resonance Raman spectroscopy and magnetic susceptibility measurement. Correlations between electronic structures and electron transfer ability are investigated in detail.

## 1. Reductive Manganese Species Related to Dioxygen Activation

The previous study has shown that a manganese(III) salen

complex mediates  $\text{O}_2$  activation in the presence of  $\text{OH}^-$  from 2 M KOH aqueous solution.<sup>1)</sup> This study investigated an active species that is responsible for dioxygen activation in this reaction. Then, the reaction of a manganese(III) salen complex with  $\text{Bu}_4\text{NOH}$  was carefully carried out at low temperature ( $-80\text{ }^\circ\text{C}$ ). It was found that a new species with characteristic visible absorptions is generated. Cyclic voltammetry shows that the Mn(III)/Mn(IV) redox of the new species appears at  $-0.31\text{ V vs Fc/Fc}^+$ , which is drastically lower than that of the starting manganese(III) complex by 1.13 V. According to the  $^1\text{H}$  and  $^2\text{H}$  NMR spectra, the new species is assigned as a six-coordinate anionic  $[\text{Mn}^{\text{III}}(\text{salen})(\text{OH})_2]^-$  complex. Magnetic susceptibility measurements show the spin state is changed from  $S = 2$  for the starting complex to  $S = 1$  for the new species.

### Reference

1) T. Kurahashi, *Inorg. Chem.* **54**, 8356–8366 (2015).