CHEMISTRY LETTERS, pp. 917-920, 1993.

Interaction between Metal Compounds and Dioxygen Molecule in the Presence of Aliphatic Aldehydes

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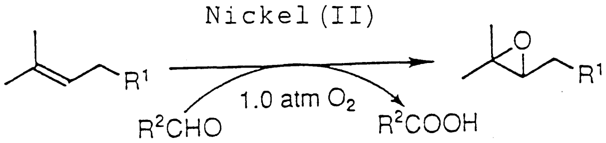
We have obtained the electrochemical evidence for the enhanced interaction between dioxygen molecule and the metal compounds such as manganese(II) and nickel(II) complexes in the presence of cyclohexanecarboxyaldehyde.

Very recently, Mukaiyama et al.[1)] have reported that in the presence of a catalytic amount of nickel(II) or manganese(III) compounds, the olefins are smoothly monooxygenated into the corresponding epoxides on treatment with aliphatic aldehydes under an atmospheric pressure of dioxygen at room temperature(see the equation below). Although the precise mechanism of this Mukaiyama reaction is not clear at present, we have pointed out that there should be a formation of singlet oxygen($^1\Delta_g$)-like active species in the mixture of $Ni(acac)_2 \cdot 2H_2O$ and cyclohexanecarboxyaldehyde, and proposed that this active oxygen species may be derived from the coordination of dioxygen to a nickel(II) ion in the presence of the aldehyde.[2)]



In our previous paper,[3)] we have pointed out that two peaks, which correspond to the reduction of dioxygen molecule, are observed in the cyclic voltammograms(CV) of the dioxygen-saturated [VO(salen)] or [VO(acen)] solution, and concluded that the appearance of two peaks should be attributed to the presence of an equilibrium, $O_2 + V(IV)=O \rightleftharpoons O_2{----}V(IV)=O$, and the reduction potential of the weakly coordinated dioxygen molecule in the adduct, $O_2{----}V(IV)=O$ is observed at more positive potential region than that of free dioxygen molecule, where H_2(salen) and H_2(acen) denote N,N'-bis(salicylidene)ethylenediamine and N,N'-bis(1-acetonylethylidene)ethylenediamine, respectively. In this article, we will show the CV of dioxygen molecule in the presence of both the metal compound and the aldehyde, which may give important informations on the mechanism of the Mukaiyama reaction.

As pointed out by us, the weak interaction between the metal compound and dioxygen molecule may occur in the metal compounds whose lobes of d-orbital containing the unpaired electron are spreading to the space, not surrounded by the ligand systems.4) This situation can be realized in some high-spin type manganese(II) compounds, such as trans-Mn([14]-diene-N_4)Cl_2, where ([14]-diene-N_4) represents 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, because d_{xz} and d_{yz} orbitals of this compound is not screened by the ligand system. The CV of this Mn(II) complex5) under O_2 molecule is illustrated in Fig. 1. Since the redox wave due to $\mathrm{Mn(II)} \rightleftharpoons \mathrm{Mn(III)}$ is not observed in the range +0.4 —— -1.0 V(vs. SSCE), no wave was observed in this region under an Ar atmosphere. In the presence of dioxygen molecule(see trace A in Fig. 1), two peaks at -0.83 and -0.58 V(vs. SSCE) are observed for the system containing Mn([14]-diene-N_4)Cl_2(1×10^{-3} mol dm^{-3}) and O_2(2.1×10^{-3} mol dm^{-3}).2) As the reduction peak at -0.83 V corresponds to that of free dioxygen molecule(see Table 1), the appearance of a small peak at -0.58 V indicates the presence of dioxygen molecule which is weakly interacting with a manganese(II) ion. This is supported by the fact that the peak current at -0.58 V increases with the increasing of the concentration of the added manganese(II) ion(cf. trace B in Fig. 1). The addition of cyclohexane-

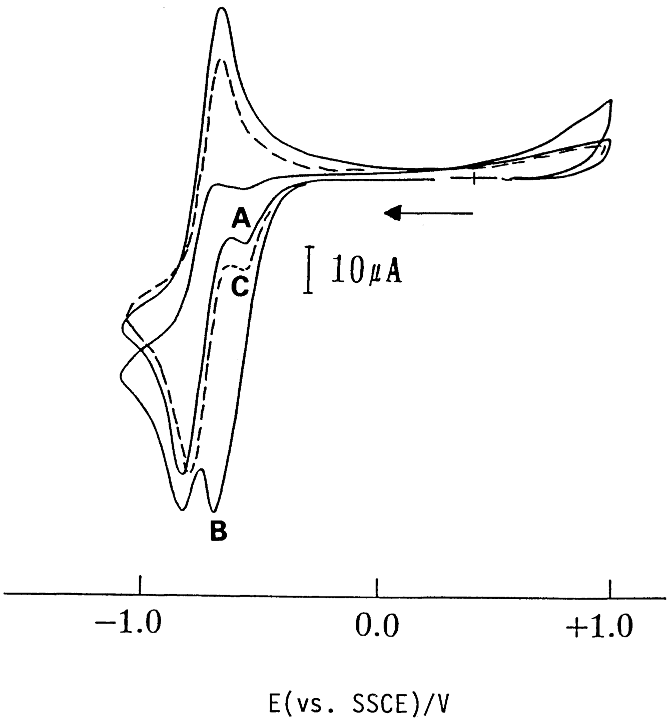


Fig. 1. CV of dioxygen in the presence of Mn([14]-diene-N_4)Cl_2 (in dmso, $[O_2]=2.1\times10^{-3}$ mol dm^{-3}, 25 °C, scan speed 100 mV/s).
A: Mn(II)(1×10^{-3} mol dm^{-3}), B: Mn(II)(5×10^{-3} mol dm^{-3}),
C: Mn(II)(1×10^{-3} mol dm^{-3})+cyclohexanecarboxyaldehyde(5×10^{-3} mol dm^{-3}).

carboxyaldehyde to this has lead to the increase of the reduction current due to the weakly interacting dioxygen, as shown in trace C in Fig. 1. This is suggesting that the interaction between the dioxygen and the manganese(II) ion is enhanced in the presence of the aldehyde in the dmso solution.

Only one peak was observed in the CV of dioxygen for the solution containing $Ni(acac)_2 \cdot 2H_2O$ or $Zn(acac)_2 \cdot H_2O$, as shown in Fig. 2, the reduction potentials being nearly the same as that of free dioxygen molecule(cf. Table 1). This shows that the interaction between dioxygen molecule and the metal ions in these compounds is negligible. When cyclohexanecarboxyaldehyde was added to the nickel(II) system, the shoulder has appeared in more positive region(see trace B in Fig. 2), but no shoulder or peak was observed for the corresponding Zn(II) system. In the case of n-heptylaldehyde, no shoulder or peak was detected for both the nickel(II) and zinc(II) systems. These seem to be in good accordance with the experimental results that $Ni(acac)_2 \cdot 2H_2O$/ cyclohexanecarboxylaldehyde system is active for the epoxidation of olefins, but

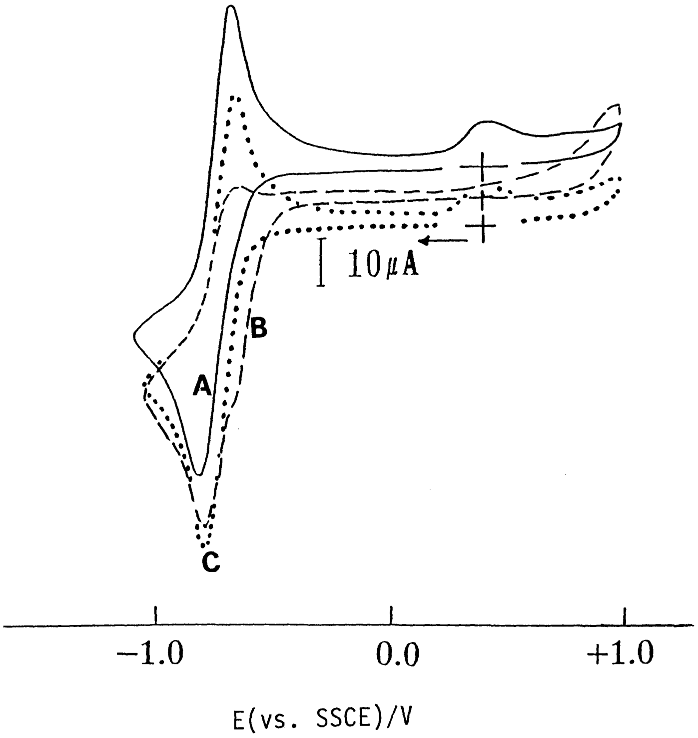


Fig. 2. CV of dioxygen in the presence of Ni(II) and Zn(II) compounds (in dmso, 25 °C, $[O_2]=2.1\times10^{-3}$ mol dm^{-3}, scan speed 100 mV/s).
A: $Ni(acac)_2 \cdot 2H_2O$(1×10^{-3} mol dm^{-3}), B: $Ni(acac)_2 \cdot 2H_2O$(1×10^{-3} mol dm^{-3}) + cyclohexanecarboxyaldehyde(4×10^{-3} mol dm^{-3}), C: $Zn(acac)_2 \cdot H_2O$(1×10^{-3} mol dm^{-3}).

Table 1. Reduction potential of dioxygen(V, vs. SSCE) in the presence of metal compounds(25 °C, in dmso, scan speed 100 mV/s)

Free dioxygen	-0.82	
Mn([14]-diene-N_4)Cl_2(1 mM)[a]	-0.83,	-0.58
+ cyclohexanecarboxyaldehyde(5 mM)	-0.80,	-0.57
Mn([14]-diene-N_4)Cl_2(5 mM)	-0.83,	-0.70
Ni(acac)$_2$•2H_2O(1 mM)	-0.83	
+ cyclohexanecarboxyaldehyde(4 mM)	-0.81,	-0.68^{sh} [b]
+ heptylaldehyde(5 mM)	-0.81	
Zn(acac)$_2$•H_2O(1 mM)	-0.83	
+ cyclohexanecarboxyaldehyde(4 mM)	-0.82	
+ heptylaldehyde(5 mM)	-0.82	

a)mM=1x10^{-3} mol dm^{-3}. b)sh=shoulder

Zn(acac)$_2$•H_2O/cyclohexanecarboxyaldehyde and Ni(acac)$_2$•2H_2O/heptylaldehyde systems are inactive for the degradation of TCPN.$^{2)}$

Based on these facts, it seems reasonable to assume that the shoulder observed at ca. -0.68 V in the Ni(acac)$_2$•2H_2O/cyclohexanecarboxyaldehyde/O_2 system is closely related with the formation of an active oxygen species in the system, as suggested in our previous paper.$^{2)}$

References

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2) Y. Nishida, T. Fujimoto, and N. Tanaka, Chem. Lett., 1992, 1291.

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4) Y. Nishida, T. Tokii, and I. Watanabe, Z. Naturforsch., B, 47, 905(1992).

5) The electrochemical measurements were performed by the usual manner; solvent, dimethyl sulfoxide(dmso); supporting electrolyte, 0.1 mol dm^{-3} (n-C_4H_9)$_4$NBF_4; 25 °C; glassy carbon electrode; reference electrode, saturated sodium chloride calomel electrode(SSCE).

(Received March 10, 1993)