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Formation of Singlet Oxygen-Like Active Oxygen Species in System Containing Nickel(II) Complex and Aliphatic Aldehyde

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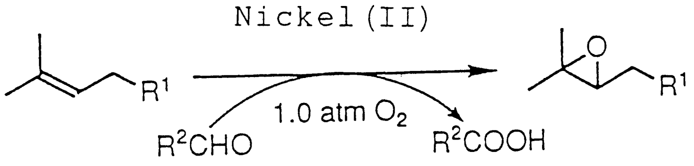
The reaction mixture of nickel(II) β-diketonato complex and aldehyde(pivalaldehyde or cyclohexanecarboxaldehyde) exhibits high reactivity toward tetraphenylcyclopentadienone(one of famous singlet oxygen ($^1\Delta_g$) scavenger), and the origin of unique reactivity of the system was discussed.

There has been much recent interest in the interpretation of the mechanism of activating of molecular oxygen by metal complexes.[1)] Very recently, Mukaiyama et al.[2)] have reported that in the presence of a catalytic amount of a bis(1,3-diketonato)nickel(II) complex, trisubstituted and exo-terminal olefins or norbornene analogues are smoothly monooxygenated into the corresponding epoxides in high yields on treatment with aldehyde under an atmospheric pressure of oxygen at room temperature. (see the equation below) They have observed that the nickel(II) complexes with β-diketones are active, whereas the planar complex, Ni(salen), is inactive to this reaction, however, they did not give any comment on the mechanism of the reaction. In this report we will show that singlet oxygen-like active species is formed in the reaction mixture of nickel(II) β-diketonate complex and aldehyde(pivalaldehyde and cyclohexanecarboxaldehyde) under an aerobic condition, and that this active oxygen species



should be a key compound for the epoxidation of olefins.

The metal compounds used in this study are Ni(acac)$_2$·2H$_2$O, Ni(dbm)$_2$ · 2H$_2$O, Ni(salen), Co(dbm)$_2$· 2H$_2$O, Cu(dbm)$_2$, Cu(salen), Cu(sal-pr^i)$_2$,3) and Zn(dbm)$_2$·H$_2$O, where H(acac), H(dbm) and H$_2$(salen) are acetylacetone, dibenzoylmethane, and N,N'-bis(salicylidene)ethylenediamine, respectively. It is well known that tetraphenylcyclopentadienone (hereafter abbreviated as TCPN) is one of the singlet oxygen ($^1\Delta_g$) quencher, and shows strong absorption band at 507 nm;it reacts with the singlet oxygen to yield the corresponding peroxide with decoloration.4) In a typical run, to the 1,2-dichloroethane solution (50 mℓ) of TCPN (1/1500 M), were added metal complex (0.02-0.13 mmol) and aldehyde (0.5-4 mℓ), and the time course of the absorbance at 507 nm of the solution was measured at 25 ℃, the results being illustrated in Fig. 1. As shown in Fig. 1, the absorbance at 507 nm

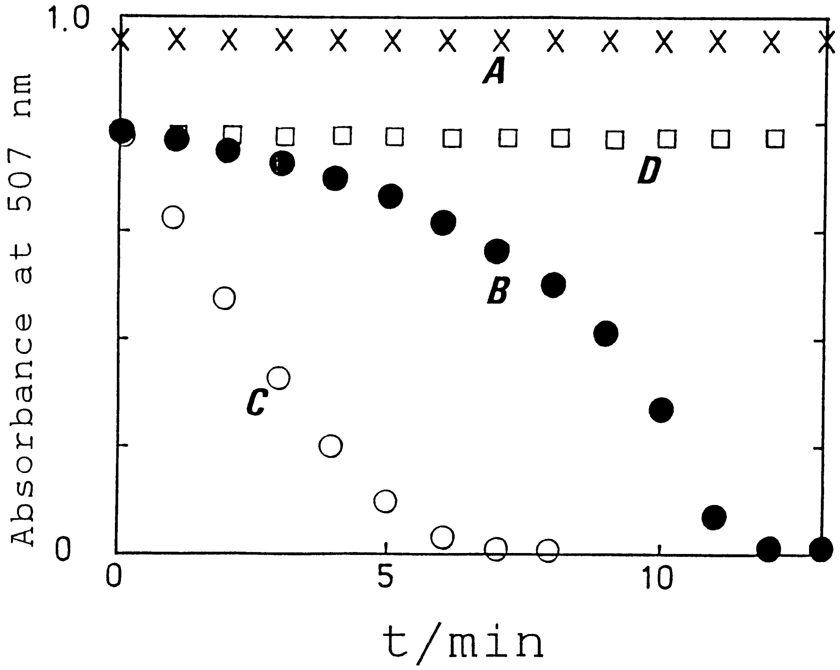


Fig. 1. Time course of absorbance at 507 nm of reaction mixture (see text).

A: Ni(salen) (0.033 mmol) and cyclohexanecarboxaldehyde (0.5 mℓ)
B: Ni(acac)$_2$ (0.033 mmol) and cyclohexanecarboxaldehyde (0.5 mℓ)
C: Ni(acac)$_2$ (0.132 mmol) and cyclohexanecarboxaldehyde (2.0 mℓ)
D: Ni(acac)$_2$ (0.033 mmol) and n-heptylaldehyde (1.0 mℓ)

rapidly decreased in the solution containing Ni(acac)$_2$ and cyclohexanecarboxaldehyde, but no decrease of the absorbance was detected in the mixture with Ni(salen) under the same experimental conditions. Similar decrease of the absorbance at 507 nm was also observed for the systems containing pivalaldehyde, however, the decrease of the absorbance was negligible in the solution containing a linear aliphatic aldehyde, such as n-heptylaldehyde(cf. Fig. 1). These are all in good accordance with the results reported by Mukaiyama,$^{2)}$ e.g., nickel(II) β-diketonato complex exhibits high activity for olefin epoxidation in the presence of aldehydes (pivalaldehyde and cyclohexanecarboxaldehyde), but its activity of Ni(salen) is negligible, and also the activity of the nickel(II) complexes for olefin epoxidation depends on the aldehydes used; the yield of the epoxides is much lower in the case of linear aliphatic aldehyde than that in the system of the α-branched aliphatic aldehydes. Since the TCPN is the quencher of singlet oxygen($^1\Delta_g$), it seems reasonable to assume that the formation of singlet oxygen-like active oxygen species is a key point in the epoxidation of olefin by the bis(1,3-diketonato)nickel(II)/aldehyde system.

We also have found the following facts; the cobalt(II) β-diketonate/aldehyde(α-branched aldehydes) systems are active to the formation of an active oxygen species, however, the corresponding zinc(II) β-diketonates are inactive. The bis(1,3-diketonato)copper(II) compounds and square planar complexes such as Cu(salen) are inactive, and the activity of distorted tetrahedral complexes, such as Cu(sal-pr^i)$_2$ is much low.

The activity of the bis(1,3-diketonato)nickel(II)/aldehyde system is dependent on the solvent used; Ni(acac)$_2$·2H$_2$O/pivalaldehyde system in 1,2-dicholoroethane is highly active, but the same system in 1,2-dichloroethane/N,N-dimethylformamide(=4/1, v/v) is almost inactive to the transformation of TCPN. Based on these facts, it seems reasonable to assume that the coordination of aldehyde to the nickel(II) ion in bis(1,3-diketonato)nickel(II) is the most important process for the formation of an active oxygen species, and that the formation of the active oxygen species may occur through the coordination of dioxygen to the nickel(II) atom, as shown in Fig. 2. The coordination of aldehyde to a nickel(II) ion, which leads to the increase of electron density on the nickel(II) atom, may promote the coordination of dioxygen to the nickel(II) atom. These may be consistent with the fact that α-branched aldehyde exhibits much higher activity for olefin epoxidation, the results obtained in this work, and also with the experimental fact that the more oxidizable the nickel(II) ion is, the higher the catalytic activity for epoxidation of olefin is.5) It is well known that the coordinated dioxygen molecule exhibits unique reactivity,6) similar to that of the metal peroxides. The present authors have proposed that the unique reactivity observed should be due to that the coordinated dioxygen molecule contains more or less degree of singlet oxygen character,7) which may be supported by the theoretical study reported by Newton and Hall.8) Thus, it seems reasonable to consider that the olefin epoxidation in nickel(II)/aldehyde system may proceed through the reaction between olefin and the activated dioxygen molecule with singlet oxygen character.

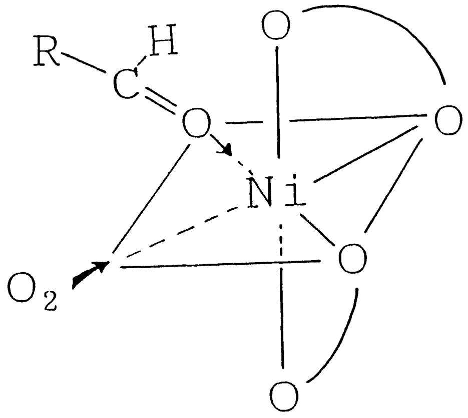


Fig. 2. Assumed scheme for activation of dioxygen in bis(1,3-diketonato)nickel(II)/aldehyde system.

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