

Radical-chain auto-oxidation of cyclohexene initiated by superoxide ion coordinating to Cr(III)porphyrin

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(Received August 28, 2006; Accepted October 16, 2006)

Abstract

Air oxidation of cyclohexene to cyclohexene oxide, 2-cyclohexene-1-one and 2-cyclohexene-1-ol proceeded using 5,10,15,20-tetraphenylporphyrinatochromium(III)chloride (Cr(III)(tpp)Cl) as a metalloporphyrin and insoluble zinc powder as a reductant. The role of Cr(tpp)Cl was investigated by adding 1-methylimidazole (1-MeIm) and 3,5-di-*tert*-butyl-*p*-hydroxyl-toluene (BHT) to this system. In this oxidation mechanism, a superoxide ion coordinating to Cr(III)(tpp)Cl was first produced via the reduction process of the Cr(III) porphyrin-O₂ coordination compound to Cr(II)porphyrin-O₂ compound by zinc powder, and second, the superoxide ion coordinating to Cr(III)(tpp)Cl abstracted hydrogen from one of two allyl positions of cyclohexene, initiating radical-chain auto-oxidation.

Key words: Cr porphyrin, radical-chain auto-oxidation, activated superoxide ion

1. Introduction

Many attempts have been made using metalloporphyrin as a model complex, in order to elucidate the activity of a monooxygenase such as cytochrome P-450. Many model systems were roughly divided into two types according to the method of generation of active oxygen species. In one type, the system contains an activated dioxygen molecule produced by reducing O₂ with a metal porphyrin and a reducing agent as well as an activating reagent such as benzoic anhydride[1-5]. In the other type, the system contains an oxygen donor (such as iodosylbenzene

and hydrogen peroxide) and a metal porphyrin[6]. An active high-valence oxometalloporphyrin complex is an important intermediate in both types of systems, because it produces oxidation products by reacting with the substrate. We have reported the dioxygen-activated reductive epoxidation of cyclohexene (**1**) using Mn(III)porphyrin as the catalyst, zinc powder as the reductant and benzoic anhydride as the activating reagent[3,4]. On the other hand, the superoxide ion (O₂⁻), obtained by reducing O₂ with Co(II)porphyrin, abstracted hydrogen from aldehyde, and also added to the double bond of olefin,

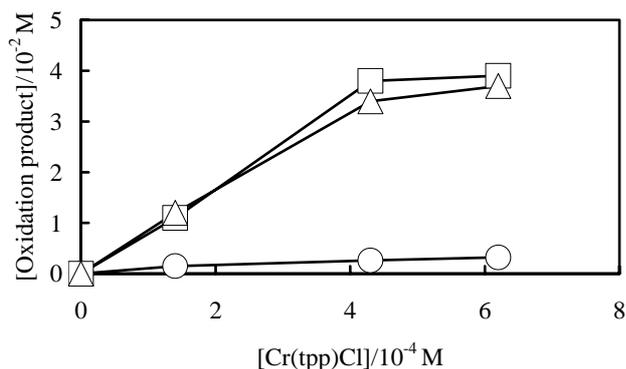
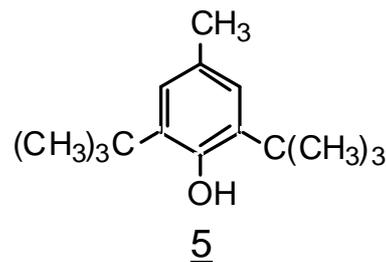


Fig.1 Dependence of amount of oxidation products (epoxide (2) (□), 1-one (3) (△), and 1-ol (4) (○)) on concentration of Cr(tpp)Cl in air-equilibrated acetonitrile suspension containing 7.3×10^{-2} M zinc powder and 0.47 M cyclohexene at 30°C (reaction time: 24 hr).

cyclohexene was obtained after stirring its solution for 24 hr, oxidation products such as cyclohexene oxide (epoxide) (2), 2-cyclohexene-1-one (1-one) (3), and 2-cyclohexene-1-ol (1-ol) (4) were obtained as the oxidation products of cyclohexene by adding Cr(III)(tpp)Cl into this system. The dependence of amount of the oxidation products on the concentration of Cr(III)(tpp)Cl, [Cr(tpp)Cl], is shown in Fig. 1. The amount of the oxidation products saturated above 4.3×10^{-4} M Cr(tpp)Cl. Electronic absorption spectra of the reacting solution showed a disappearance of Cr porphyrin after the oxidation reaction.

Because allylic oxidation products such as 1-one (3) and 1-ol (4) were obtained as the main products, this oxidation may proceed by a radical reaction in which hydrogen abstraction from allyl positions of cyclohexene (1) is the initiation reaction[12]. No oxidation product was obtained when either O₂ or zinc powder was not included. However, even when the oxidation reaction proceeded under optimum conditions, the amount of zinc consumed was extremely slight, and could not be determined. These results suggest that Cr(tpp)Cl acts not as a catalyst but as an initiator for producing a species which



causes the radical-chain reaction. Since the selectivity of epoxide (2) was considerably smaller in our system (3%) than in the Co(II)porphyrin system (13%) reported by Ohkatsu and Tsuruta[8], the initiation reaction mechanism may be different between the two systems, although the radical-chain reaction is involved in these oxidation reactions.

3,5-Di-*tert*-butyl-*p*-hydroxyl-toluene (BHT) (5) was added to this system as a radical inhibitor, to examine whether this oxidation reaction was a radical reaction or not. The dependence of the amount of oxidation products on the concentration of BHT (5), [BHT], is shown in Fig. 2. Since the amount of oxidation products decreased abruptly upon adding a slight amount of BHT, it was confirmed that this oxidation is a radical reaction, although the effect of BHT as a radical inhibitor must be discussed carefully.

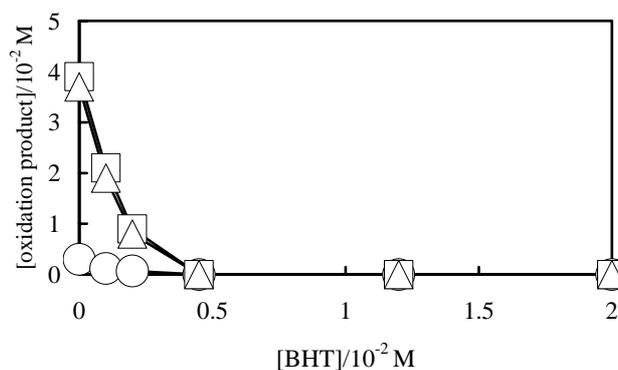


Fig.2 Effect of addition of BHT (5) on the amount of oxidation products (epoxide (2) (□), 1-one (3) (△), and 1-ol (4) (○)) in an air-equilibrated acetonitrile suspension containing 4.3×10^{-4} M Cr(tpp)Cl, 7.3×10^{-2} M zinc powder, and 0.47 M cyclohexene at 30°C (reaction time: 24 hr).

It has been reported that in the dioxygen-activated

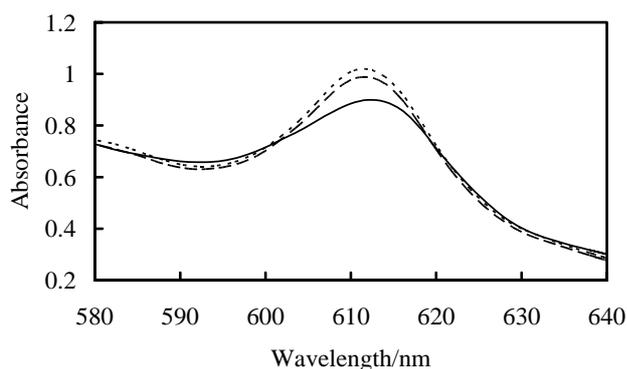


Fig.3 Effect of addition of 1-MeIm on electronic absorption spectra of $1.0 \times 10^{-4} \text{M}$ Cr(tpp)Cl in acetonitrile solution at room temperature. Concentration of 1-MeIm: 0M (solid line), $0.5 \times 10^{-4} \text{M}$ (broken line), and $1.0 \times 10^{-4} \text{M}$ (dotted line).

reductive epoxidation of olefin using Mn(III) porphyrin catalyst, the coordination of dioxygen to Mn(II)porphyrin was prevented by the addition of a large amount of nitrogen base such as 1-MeIm, which inhibits the epoxidation of olefin[2,4]. A similar effect of ligands has been reported in the system in which a superoxide ion produced via the Co(II)porphyrin- O_2 coordination compound initiation of the auto-oxidation of aldehyde[13]. Hence, 1-MeIm was added to our oxidation system to examine whether the coordination of dioxygen to Cr porphyrin is essential or not. Fig. 3 shows the dependence of the electronic absorption spectra of Cr(III)(tpp)Cl on [1-MeIm] in an acetonitrile solution. The electronic absorbance at the absorption peak of 610 nm obtained in Cr(III) porphyrin acetonitrile solution rapidly increased upon the addition of 1-MeIm until the molar ratio of [1-MeIm] to [Cr(III)(tpp)Cl] became unity where the absorption spectra showed an isosbestic point at around 602 nm, but the absorbance did not increase at all with any further addition. This result indicates that the 1-MeIm readily coordinates to Cr(III) ions in Cr(III)(tpp)Cl, and the Cr(III)porphyrin exists only as Cr(III)(tpp)(Cl)(1-MeIm) even when the molar ratio of [1-MeIm] to [Cr(III)(tpp)Cl] is more than unity in

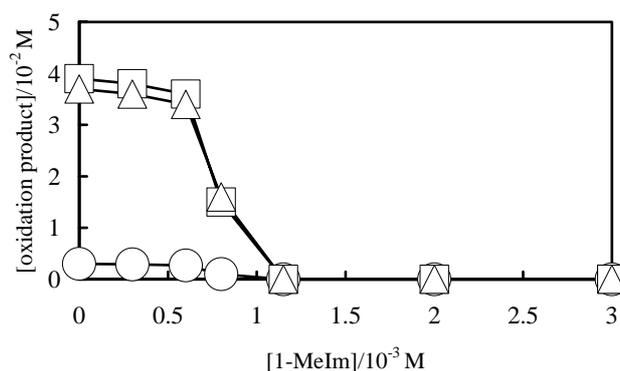
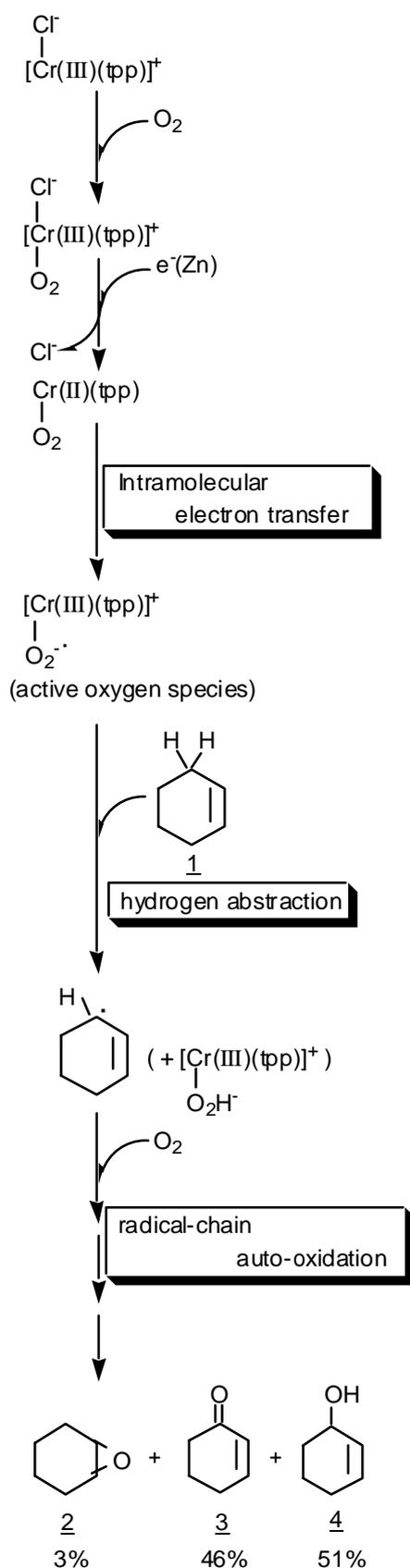


Fig.4 Effect of addition of 1-MeIm on amount of oxidation products (epoxide (2) (○), 1-one (3) (△), and 1-ol (4) (□)) in air-equilibrated acetonitrile suspension containing $4.3 \times 10^{-4} \text{M}$ Cr(tpp)Cl, $7.3 \times 10^{-2} \text{M}$ zinc powder, and 0.47M cyclohexene at 30 °C (reaction time: 24 hr).

the solution[14]. Fig. 4 shows the dependence of the amount of oxidation products on [1-MeIm]. The amount of oxidation products was decreased considerably by such a coordination. These results suggest that the coordination of dioxygen to Cr(III)porphyrin is essential for the formation of active oxygen species such as superoxide ion [7,8,13].

Cr(III/II) and $\text{O}_2/\text{O}_2^{\cdot -}$ pairs showed $E_{1/2}$ values of -1.4V vs Fc^+/Fc and -1.3V in the acetonitrile solution, respectively. The standard redox potential of the Zn^{2+}/Zn pair is -1.5V vs Fc^+/Fc in the acetonitrile solution[15]. Although zinc powder can thermodynamically reduce O_2 to $\text{O}_2^{\cdot -}$, the oxidation of cyclohexene did not proceed in the system without Cr(tpp)Cl. The reason for this may be either that the reduction of O_2 to $\text{O}_2^{\cdot -}$ by zinc powder is very slow or free $\text{O}_2^{\cdot -}$ does not exhibit the initiation activity for the oxidation, where free $\text{O}_2^{\cdot -}$ means that $\text{O}_2^{\cdot -}$ is not bound by the coordination to Cr(tpp)Cl. Furthermore, Co(II)(tpp) and Mn(II)(tpp) did not exhibit the initiation activity under the experimental conditions adopted in this study. That is, our air-oxidation system for cyclohexene (1) is reactive compared with the other systems.



In summary, the coordination of dioxygen to Cr(III)(tpp)Cl occurs first in the oxidation of cyclohexene(1). Next, the reduction of the Cr(III)(tpp)Cl-dioxygen coordination compound (Cr(III)(tpp)Cl-O₂) to Cr(II)(tpp)-O₂ proceeds in the presence of zinc powder, and subsequently, Cr(III)(tpp)-O₂⁻ is formed by intramolecular electron transfer from the Cr(II)(tpp) part to the O₂ part. Although it is known that the O₂⁻ formed from Co(II)(tpp)-O₂ adduct has electrophilic reactivity[8], we believe that the binding O₂⁻ in Cr(III)(tpp)-O₂⁻ has nucleophilic reactivity because of the large electron-donating power of Cr(II)(tpp), and the binding O₂⁻ abstracts hydrogen from one of the two allyl positions of cyclohexene (1), thus initiating the radical-chain auto-oxidation. The system proposed in this study is summarized in Scheme 2.

Acknowledgements

We wish to thank Professor Syuichi Matsui (Fukui National College of Technology, Japan) for helpful suggestions and discussion.

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Cr(III)ポルフィリンを用いたシクロヘキセンの自動酸化

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要旨

空気飽和のアセトニトリル中において、シクロヘキセンの 2-シクロヘキセン-1-オール、2-シクロヘキセン-1-オンおよび、シクロヘキセンオキシドへの酸化反応が、金属ポルフィリン化合物としてテトラフェニルポルフィリナト Cr(III)塩化物 (Cr(III)(tpp)Cl)、および還元剤として Zn 粉末を添加することにより進行した。Cr ポルフィリンの役割が、1-メチルイミダゾール(1-MeIm)及び 3,5-ジ-*tert*-ブチル-*p*-ヒドロキシトルエン (BHT)の添加により検討された。この酸化反応では、酸素分子がまず Cr(III)ポルフィリンの Cr(III)イオンに配位し、その後、Zn 粉末により Cr(III)イオンが Cr(II)イオンに還元され、さらに分子内電子移動により Cr(III)イオンに配位したスーパーオキシドイオン(O₂⁻)が生成し、その Cr(III)イオンに配位した O₂⁻がシクロヘキセンのアリル位から水素原子を引き抜いて反応が開始される。その後、ラジカル連鎖自動酸化反応が引き続き起ると推定された。

キーワード : Cr ポルフィリン、ラジカル連鎖自動酸化、スーパーオキシドイオン