CHEMISTRY LETTERS, pp. 625-628, 1988.

Photochemical Epoxidation of Olefins with Molecular Oxygen Activated by Oxo(tetra-p-tolylporphinato)molybdenum(V)

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Photochemical epoxidation of olefins was catalyzed by a molybdenum porphyrin in benzene under aerobic conditions. The catalytic reaction rate was somewhat lower than that observed for the similar reaction catalyzed by the corresponding niobium complex. A reaction mechanism, involving cooperative interaction of an olefin and dioxygen with the molybdenum(IV) species, was postulated.

Metalloporphyrins have attracted a great deal of attention in connection with photochemical energy conversion systems, oxygen carriers, and specific oxygenation catalysts. We have already prepared porphyrin complexes of early transition metals and investigated their redox behavior by electrochemical means.1) We have also reported on the photochemical redox behavior of niobium2) and molybdenum3) porphyrins. The tri-μ-oxo dimer of (tetra-p-tolylporphinato)niobium(V) is reduced upon irradiation with the visible light along with the homolytic cleavage of one of the bridging Nb-O bonds to afford the Nb^{IV} species. The reduced niobium species is subjected to rapid reoxidation with atmospheric molecular oxygen, affording an oxygenated complex, $Nb^{V}(O)(OO^{\cdot -})(ttp)$, where ttp stands for the tetra-p-tolylporphinato ligand. The oxygenated complex oxidizes olefins to give exclusively the corresponding epoxides.4) The above catalytic system is considered to be an efficient functional model of cytochrome P-450 and provides a useful guidepost for development of selective epoxidation catalysts. We report here on the epoxidatio

Table 1. Aerobic epoxidation of olefins upon irradiation with the visible light at 22 °C[a)]

Olefin	Irradiation time/h	Yield/%[b)]
Cyclohexene (2 mL)	12	8100
2-Hexene (2 mL)	12	2400
1-Hexene (2 mL)	12	0
1,4-Hexadiene (2 mL)	12	0[c)]

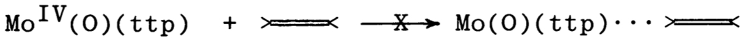
a) Benzene (2 mL) was used as the solvent. b) Yield based on the initial amount of the catalyst, $Mo^V(O)(OEt)(ttp)$. c) Neither 1,2-epoxy-4-hexene nor 4,5-epoxy-1-hexene was detected.

while Nb^V is displaced by ca. 1 Å from the ligand plane.[6)] Terminal olefins, 1-hexene and 1,4-hexadiene, did not undergo reaction under the present conditions, and precipitation of the dimer complex, $Mo^V(O)(ttp)$-O-$Mo^V(O)(ttp)$, was observed. Thus, even though the terminal olefins may interact with the catalyst quite readily, the resulting intermediate must afford the dimer complex more readily than the oxygen transfer from the intermediate to olefins. The reaction did not proceed under the following conditions; without irradiation with the visible light, under deoxygenated atmosphere, or without addition of complex **1** to the reaction system. The reaction deceased upon interruption of irradiation. This apparently indicates that the reaction does not take place via a chain mechanism affording subsequent radical species.

The photochemical reaction of complex **1** was examined under various conditions by means of electronic spectroscopy. Complex **1** shows absorption bands at 452, 580, and 620 nm in benzene or the same solvent containing 1%(v/v) ethanol (Fig. 1), which decreased in their intensities upon anaerobic irradiation with the visible light, and the resulting species showed new bands at 432 and 555 nm. The latter species was assigned to $Mo^{IV}(O)(ttp)$.[2)] The reaction is referred to photoreduction of the central metal atom caused by homolysis of the axial coordinate bond as represented by Eq. 1. The ethoxy radical presumably undergoes disproportionation in a bimolecular process to afford ethanol and acetaldehyde, because the radical species did not initiate a chain reaction as mentioned above.

$$Mo^V(O)(OEt)(ttp) \xrightarrow{h\nu} Mo^{IV}(O)(ttp) + EtO\cdot \qquad (1)$$

The reaction processes were investigated by ESR spectroscopy. Complex **1** has one d-electron and shows a strong ESR signal, which decreased in its intensity upon anaerobic irradiation with the visible light in benzene or the same solvent containing 1%(v/v) ethanol.[3)] Similar ESR behavior was observed for the photoreduction of complex **1** in benzene containing cyclohexene or 2-hexene as the substrate upon anaerobic irradiation at 22 °C. The reduced species, $Mo^{IV}(O)(ttp)$, remained unchanged under anaerobic conditions. The absorption spectrum of the Mo^{IV} species did not undergo any change in its band shape and intensity for several days in the presence or absence of olefins under anaerobic conditions at 22 °C. These observations indicate that the substrate species hardly interacts with the reduced complex, $Mo^{IV}(O)(ttp)$ (Eq. 2).



(2)

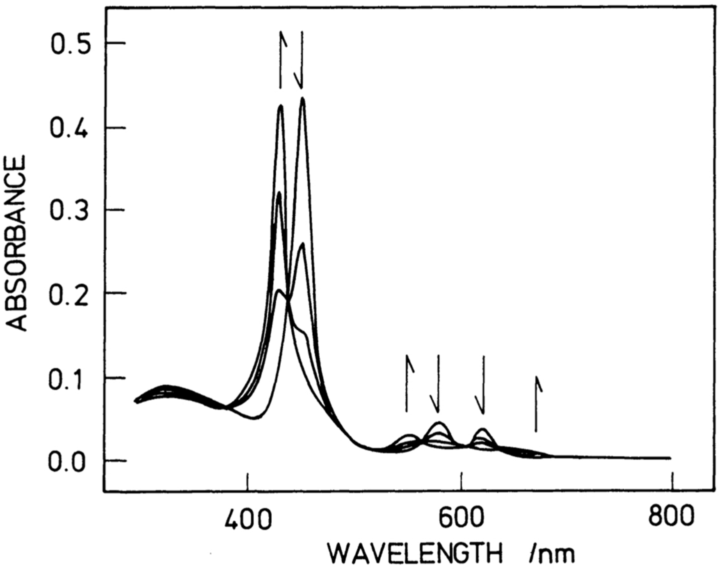


Fig. 1. Electronic spectral change observed for $Mo^{V}(O)(OEt)$-(ttp) (3.03×10^{-4} mol dm^{-3}) in benzene at 22 °C under aerobic irradiation conditions; a 500-W tungsten lamp from a distance of 20 cm. The above reaction sample was diluted with benzene by a hundred-fold for the spectral measurements. Spectra shown here were taken at time intervals of 0, 15, 30, and 45 min. The identical spectral change was observed under anaerobic conditions at a larger rate.

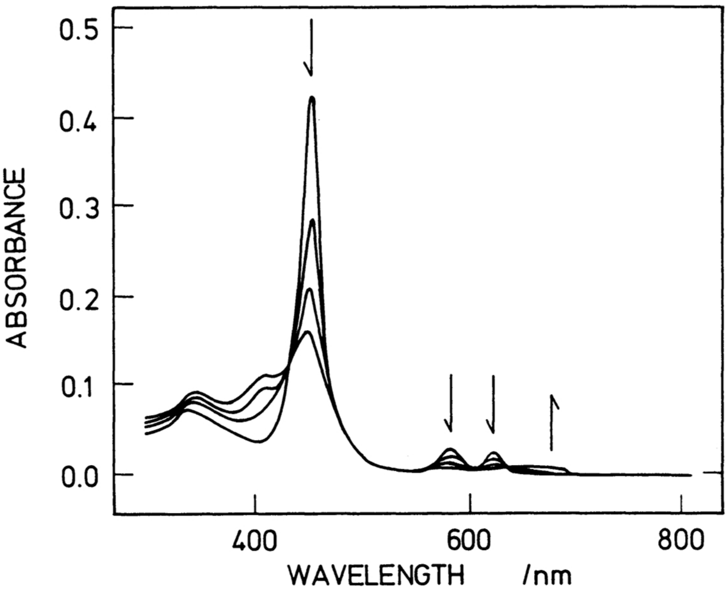


Fig. 2. Electronic spectral change observed for a mixture of $Mo^{V}(O)(OEt)(ttp)$ (3.03×10^{-4} mol dm^{-3}) and cyclohexene (2.46 mol dm^{-3}) in benzene at 22 °C under aerobic irradiation conditions; a 500-W tungsten lamp from a distance of 20 cm. The above reaction sample was diluted with benzene by a hundred-fold for the spectral measurements. Spectra shown here were taken at time intervals of 0, 15, 30, and 45 min.

$Mo^{IV}(O)(ttp)$, generated upon anaerobic conditions in benzene or the same solvent containing 1%(v/v) ethanol, was reoxidized when exposed to air. The 432-nm band disappeared along with re-appearance of the bands due to complex **1**. The reaction rate for photochemical reduction of complex **1** under aerobic conditions was found to be smaller than that observed under anaerobic conditions due to the reoxidation reaction, even though the spectral behavior was identical with each other under both aerobic and anaerobic conditions (Fig. 1).

Since significant shifts in the visible absorption bands were not detected upon addition of an olefin to the benzene solution of complex **1** without irradiation, the possible formation of an intermediate via interaction of the substrate with the Mo^{V} complex is ruled out. In addition, a reaction pathway involving formation of an intermediate oxygen-adduct, which would be obtained via interaction of dioxygen with the reduced complex (Eq. 3), is also excluded, since an additional absorption band due to such species was not observed under aerobic irradiation conditions.

$$Mo^{IV}(O)(ttp) + O_2 \xrightarrow{\quad \times \quad} Mo^{V}(O)(OO^{\overline{\cdot}})(ttp) \qquad (3)$$

Aerobic irradiation of complex **1** in benzene containing the reactive olefin resulted in somewhat different spectral change as illustrated in Fig. 2, and the absorption bands due to the Mo^{IV} species were not detected under these conditions. The new absorption bands observed in this spectrum must be originated from the reaction intermediate. In reference to the spectral behavior illustrated in Figs. 1 and 2, complex **1** was consumed in the initial epoxidation step at a rate comparable to that for the formation of the Mo^{IV} species without the substrate. This indicates that the Mo^{IV} species undergoes reaction quite rapidly with dioxygen and the substrate without its accumulation. Consequently, the present catalytic reaction proceeds most plausibly via cooperative interaction of the substrate and dioxygen with the reduced molybdenum.

The detailed mechanisms involved in oxygen-transfer from the intermediate to the reactive olefin and regeneration of the catalyst are under investigation in our laboratories.

The present work was supported in part by a Grant-in-Aid for Scientific Research (No. 61550597) from the Ministry of Education, Science, and Culture.

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(Received January 5, 1988)