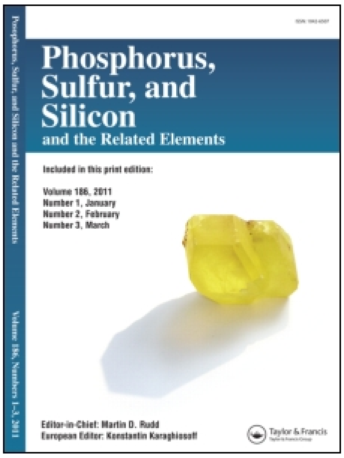

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Formation of a New Active Oxidizing Species in Photosensitized Oxygenation of Heteroatom Compounds

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FORMATION OF A NEW ACTIVE OXIDIZING SPECIES IN PHOTOSENSITIZED OXYGENATION OF HETEROATOM COMPOUNDS

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Abstract Singlet oxygen oxidation of heteroatom compounds caused cooxidation of olefin epoxides. A persulfoxide intermediate generated in singlet oxygen oxidation of sulfide can transfer an oxygen atom to iron(III) porphyrin to form the iron oxo species. A phosphadioxirane is proposed as the labile intermediate formed in singlet oxygen oxidation of phosphite. These active oxidizing species are responsible for epoxidation of olefins.

INTRODUCTION

In singlet oxygen oxidation of the designed sulfur compounds, the active oxidizing species are much stronger than singlet oxygen itself and primary intermediates such as persulfoxide and thiadioxirane are formed as secondary intermediates, which can oxidize olefin to epoxide.[1-4] In this presentation, an oxygen atom transfer from a persulfoxide to iron(III) porphyrin to form the iron oxo species,[5] which is employed for the cytochrome P-450 model system,[6] is presented. The current research interests in photosensitized oxygenation of organophosphorus[7] and organoselenium[8] compounds are also reported.

FORMATION OF NEW ACTIVE OXIDIZING SPECIES

Metalloporphyrin-Catalyzed Cooxidation of Olefin in Singlet Oxygen Oxidation of Sulfide[5]

Singlet oxygen oxidation of sulfides is responsible for the loss of activity of several important enzymes which are damaged in photodynamic action. Much attention has been devoted to the structures and reactivities of initially formed reactive intermediates such a persulfoxide and thiadioxirane intermediates. Meanwhile, a high-valency iron oxo species as an active oxidant in the cytochrome P-450 mediated monooxygenases is though to be involved in the model system employing iron(III) porphyrin and chemical oxidants such as iodosylbenzene and peracids. To our knowledge, no interaction between a sulfide-oxygen adduct and metal ion, however, has been known so far. We show here the first example of an oxygen atom transfer from a peroxidic intermediate generated in singlet oxygen oxidation of sulfide to metal ion affording metal oxo species, which is responsible for epoxidation of olefins. Actually, the primary persulfoxide intermediate if diethyl sulfide is likely to transfer an outer oxygen atom to Fe(TPFP) to afford $Fe^{IV}=O(TPFP)^{+\cdot}$, which can oxidize olefin and sulfide to epoxide and sulfoxide; Fe(TPFP) = tetrakis(pentafluorophenyl)-iron(III) chloride.

Cooxidation of Olefin in Singlet Oxygen Oxidation of Phosphite[7]

The reaction of singlet oxygen with cyclic phosphite, 1-methyl-4-phospha-3,5,8-trioxa-bicyclo[2.2.2]octane, in the presence of olefin caused cooxidation of olefins to epoxides in substantial yields. On the basis of the mechanistic investigations, the primary peroxidic intermediate is likely to transfer an oxygen atom electrophilically to olefin and sulfide to afford epoxide and sulfoxide. Therefore, it might be concluded that the labile intermediate formed in singlet oxygen oxidation of the cyclic phosphite is a phosphadioxirane having three membered-structure. This is also a first example for efficient epoxidation of olefins by the active oxidizing species generated in singlet oxygen oxidation of organophosphorus compounds.

Singlet Oxygen Oxidation of Organoselenium Compounds[8]

Singlet oxygen oxidation of dialkyl and alkyl aryl methanol affords the corresponding selenoxides, similar to the case with sulfides. Interestingly, diaryl selenides are also oxygenated in methanol. Oxygenation of benzyl-substituted selenides, however, gives benzaldehyde and diselenide instead of Se-oxygenated product. The initial formation of a perselenoxide intermediate might be conceivable. Reactivity of selenides toward singlet oxygen fairly resembles that of sulfides.

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