



Dioxygen insertion into iron(III)-carbon bonds : NMR studies of the formation and reactivity of alkylperoxo complexes of iron(III) porphyrins.

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Streszczenie

The behavior of PFemCHR2 (P is a porphyrin dianion) in solution especially in the presence of dioxygen has been examined by ^2H NMR measurements. Evidence for the photolytic Fe-C bond homolysis with the formation of PFe11 is presented. Addition of dioxygen to PFeCH2R produces two unstable intermediates, PFemO2CH2R and PFemOH, which may be directly observed at low temperatures. These form and decompose through the following reactions: $\text{PFemCH2R} + \text{O2} \rightarrow \text{PFemO2CHR2}$; $\text{PFemO2CHR2} \rightarrow \text{PFemOH} + \text{G=CR2}$; $2\text{PFemUIOH} \rightarrow \text{PFem,nOFemP} + \text{H2O}$. The formation of the product aldehyde or ketone has been established for methyl, ethyl, isopropyl, α -propyl, and benzyl ligands axially coordinating iron. The dioxygen insertion is retarded by the coordination of TV-methylimidazole to the sixth iron coordination site or by employing a sterically encumbered porphyrin. PFemOH catalyzes the decomposition of ethyl hydroperoxide to give acetaldehyde as the major organic product.

Adres publiczny

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