Catalysis of Autoxidation by Metalloporphyrins

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Summary Autoxidation of olefins and other active methylene compounds by iron(III) *meso*-tetraphenylporphin proceeds readily at 25° *via* a free-radical chain process.

There has been much recent interest in the oxidation–reduction reactions of iron porphyrin systems involving radical intermediates.[1] We report that reaction of cyclohexene and iron(III) *meso*-tetraphenylporphin chloride, $Fe^{III}(TPP)Cl$[2], by shaking under oxygen at 25 °C results in a free-radical autoxidation. Other active methylene compounds also undergo autoxidation. In a typical experiment (12 h; 25°) cyclohexene (74 mmol) and catalyst (0·006 mmol) resulted in a total oxygen uptake of 14·7 mmol. Cyclohex-2-enol (2·1 mmol), cyclohex-2-enone (9·4 mmol), cyclohexene oxide (0·4 mmol), and an undetermined amount of water were obtained. In a control experiment (12 h; 25°), in the absence of catalyst, only 0·1 mmol of oxygen uptake was observed. In the presence of catalyst there is a 2—3 h induction period after which time the $Fe^{III}(TPP)Cl$ is rapidly transformed into the oxygen-bridged dimer $[Fe^{III}(TPP)]_2O$.[3]

Other metalloporphyrins such as $Co^{II}(TPP)$,[4] $Rh^{III}[CO]$-$(TPP)Cl$,[5] and $Rh^{III}(TPP)Cl$[6] also catalyse the oxidation of cyclohexene. However, these catalysts produce a substantial amount of cyclohexene hydroperoxide; in the case of $Rh^{III}(CO)(TPP)Cl$ the hydroperoxide is the sole product of oxidation. Other active methylene compounds are also oxidized by $Fe^{III}(TPP)Cl$ as shown in the Table.

Cyclohexene hydroperoxide is most likely an intermediate in these reactions since treatment of the hydroperoxide with $Fe^{III}(TPP)Cl$ results in a very rapid and exothermic reaction, the products of which are in identical ratios as those obtained with cyclohexene. However, $[Fe^{III}(TPP)]_2O$ is not formed in the hydroperoxide reaction. In addition, decomposition of cyclohexene hydroperoxide by $Fe^{III}(TPP)Cl$ does not initiate the oxidation of cyclohexene. The decomposition of the hydroperoxide occurs rapidly but the autoxidation still has a 2—3 h induction period. Free-radical traps such as 4-t-butylcatechol instantly quench the oxidation of cyclohexene by Fe^{III}-$(TPP)Cl$ but they have no effect upon the $Fe^{III}(TPP)Cl$-catalysed decomposition of cyclohexene hydroperoxide.

Thus if cyclohexene hydroperoxide is an intermediate in the Fe^{III}(TPP)Cl-catalysed autoxidation of cyclohexene, its decomposition does not produce any chain-carrying species.

We have found that Fe^{II}(TPP)[7] can be conveniently prepared by photolysis of Fe^{III}(TPP)Cl and azobenzene under anaerobic conditions. This is essentially the reverse of the reaction reported by Castro[1b] in which an Fe^{II} porphyrin is oxidized by alkyl halides to give an Fe^{III} porphyrin halide and alkyl radical. Fe^{II}(TPP) can also be prepared by photolysis of Fe^{III}(TPP)Cl in cyclohexene under anaerobic conditions. In a possibly related process Whitten[8] has reported on the photoisomerization of stilbene-like ligands by metalloporphyrins.

degradation of the porphyrin system. However, Castro and his co-workers[1a] have reported that various Fe^{II} porphyrins were unreactive to some 30 olefins in the absence of oxygen. They also observed that trace impurities of peroxides will lead to oxidation and degradation of the porphyrin system, and, on this basis, proposed that the observations of Tsutsui et al. were caused by peroxidic impurities in the olefins used.

These two contrasting reports can be readily resolved by our results. We have also observed oxidation and degradation of Fe^{II} porphyrins by hydroperoxides. However, the reaction of Fe^{II} porphyrins and hydroperoxides will not initiate the oxidation of olefins. Solutions of Fe^{II} por-

TABLE

Substrate	Reaction time (h)	O_2 uptake (mmol)[b]	Oxidation products[a]
Cyclohexane	12	14·7	Cyclohex-2-en-1-one (73%) Cyclohex-2-en-1-ol (24%) Cyclohexene oxide (3%)
2,3-Dimethylbut-2-ene	24	21·7	2,3-Dimethylbut-3-en-2-ol (45%) Tetramethylethylene oxide (41%) Acetone (14%)
2-Methylbut-2-ene	12	6·0	3-Methylbut-3-en-2-ol (5·7%) 3-Methylbut-3-en-2-one (9·3%) 2-Methylbut-3-en-2-ol (17·1%) Trimethylethylene oxide (20%) Acetaldehyde (11%) Acetone (20%)
Cycloheptene	15	5·2	Cyclohept-2-en-1-one (83%)
1-Methylcyclohexene	16	11·9	1-Methylcyclohexene oxide (7%) 1-Methylcyclohex-2-en-1-ol (27%) 2-Methylcyclohex-2-en-1-ol (7%) 3-Methylcyclohex-2-en-1-ol (8%) 2-Methylcyclohex-2-en-1-one (22%) 3-Methylcyclohex-2-en-1-one (29%)
Tetralin	10	9·2	α-Tetralol (14%) α-Tetralone (86%)
α-Methylstyrene	8	1·0	Acetophenone (95%)

[a] Percentages are based on a total volatile product.   [b] In each case 7μmol of Fe^{III}(TPP)Cl was employed.

When a solution of Fe^{II}(TPP) was added to cyclohexene and the mixture shaken under oxygen, the dimeric species $[Fe^{III}$(TPP)$]_2$O was immediately formed, but more importantly the induction period was eliminated. The results were identical to those obtained with Fe^{III}(TPP)Cl as catalyst. The induction period could also be eliminated by irradiating the Fe^{III}(TPP)Cl–cyclohexene solution for a short time. Finally, the results were identical when either Fe^{III}(TPP)Cl or $[Fe^{III}$(TPP)$]_2$O were used initially as catalysts.

Tsutsui et al.[9] have recently reported that when a solution of iron(II) meso-porphyrin IX dimethyl ester is treated with olefins, oxidation to a Fe^{III} porphyrin took place followed by

phyrins and olefins are quite stable in the absence of molecular oxygen. Oxidation of Fe^{II} porphyrins with concurrent oxidation of olefins readily occurs under oxygen.

No evidence could be found for complex formation between Fe^{III}(TPP)Cl and either oxygen or olefin. However, when a nitrogen base occupies the vacant position of the octahedral complex, the reaction is retarded. This at least indicates that the iron atom must be free to interact with the oxygen or the olefin present.

Similar free-radical oxidations of cyclohexene have been observed using $IrCl(CO)(Ph_3P)_2$[10] and $(Ph_3P)_3PhCl$[11] as catalysts.

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[7] No attempt was made to isolate the Fe^{II}(TPP); however, our samples had identical visible spectra in pyridine solution to those found for pure Fe^{II}(TPP): λ_{max} 425·6 (ε 184,500), 489·9(5600), 529·4(17200), and 559·7(4200) nm. Personal communication from E. B. Fleischer, University of California, Irvine.
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