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# Olefin Oxidation Catalyzed by Electron Deficient Metallo-Porphyrin

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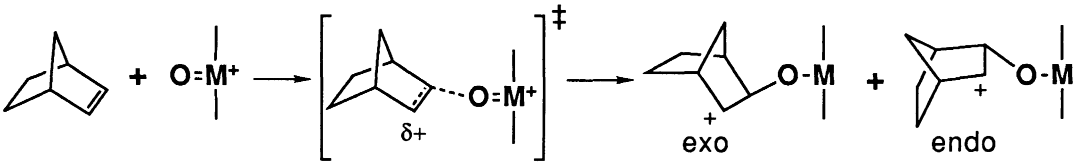
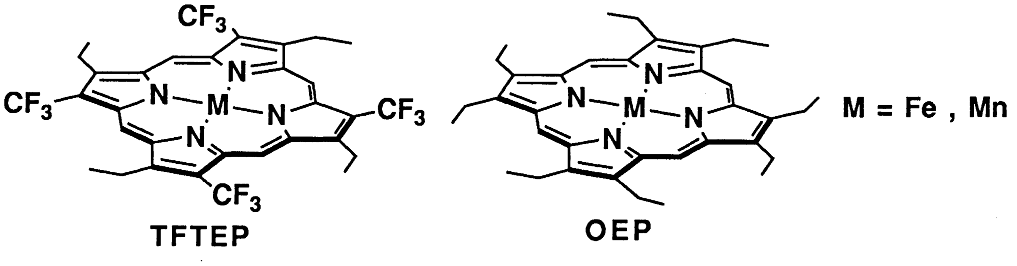
Olefin oxidations catalyzed by Fe or Mn complexes of 2,4,6,8-tetratrifluoromethyl-1,3,5,7-tetraethylporphyrin (TFTEP) using iodosobenzene as oxidant were investigated. Comparison of TFTEP with usual OEP/iodosobenzene systems shows that the electronic effect in porphyrin ring does not seriously affect the selectivity of norbornene oxidations.

Among various types of heme enzymes, cytochrome p-450 is one of the most thoroughly investigated enzymes and many mechanistic informations on this enzyme have been accumulated from biochemical and bioorganic viewpoints.[1] Recently, Traylor et al. demonstrated that the oxene species of tetraphenylporphyrin metal complex (TPP•M) having electron withdrawing groups on its phenyl rings shows unusually low exo/endo selectivity in the epoxidation of norbornene and that the ratio is clearly correlated to the electron density of a central metal of TPP derivatives. From these observations, they concluded that the oxygen atom transfer reaction from metallo oxene to olefin proceeds *via* "limited electron transfer mechanism" (Eq. 1).[2] Under these circumstances, it is interesting to investigate a reactivity of highly electron deficient porphyrin which may be expected to show an unusual "early transition state" in the olefin epoxidation. We here report the oxidation of olefins catalyzed by highly electron deficient flat porphyrin, 2,4,6,8-tetratrifluoromethyl-1,3,5,7-tetraethylporphyrin (TFTEP).[3] The results suggest that, although TFTEP shows appreciably high reactivity compared with octaethyl-porphyrin (OEP), the exo/endo selectivity does not directly reflect the electron density of the metal center in the case of present flat porphyrins.



(1)

The electron deficient character of TFTEP is clearly shown by the redox potential of its metal complex.



For example, the redox potential of TFTEP•Fe(III)Cl in $CH_2Cl_2$ is -0.07 V vs. Ag/AgCl (reversible) which is 0.3 V more positive than that of OEP•Fe(III)Cl (-0.37 V vs. Ag/AgCl). Since $CH_2Cl_2$ is known as a totally non-coordinating solvent,[4)] the present large positive shift of the redox potential of TFTEP is considered to purely reflect the electron deficiency of the central metal due to the electron withdrawing trifluoromethyl groups directly attached to the pyrrole rings. This remarkable electron deficient character of TFTEP is also reflected in the reactivity in the olefin epoxidation, i.e., in the same condition, the rate of epoxidation of cyclohexene catalyzed by TFTEP•Mn is 10 times faster than that catalyzed by OEP•Mn.[5)] Since the sterical environments of TFTEP and OEP are reasonably expected to be almost the same, this rate enhancement is also reasonably accounted for by the stronger electrophilic character of the TFTEP metal oxene intermediate due to its electron deficiency.

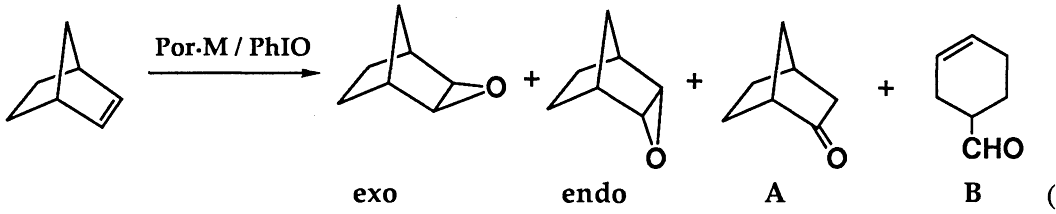
In contrast with these different properties between OEP and TFTEP, the relative reactivities of various types of olefins towards epoxidation catalyzed by these porphyrins are found to be quite similar. As shown in Table 1, the competitive reactivities standardized with 1-octene are practically the same for both Fe complexes of OEP andTFTEP and the similarity is also maintained for Mn complexes of these porphyrins. The observations strongly indicate that, though redox potentials and reactivities of these catalysts are considerably different, the present epoxidation reactions proceed *via* same oxene intermediates which are generated by the reaction of iodosobenzene with metallo porphyrins.

Table 1. The Competitive Reactivities for Olefin Epoxidation Catalyzed by TFTEP and OEP Metal Complexes[a)]

| Porphyrin | Relative rates[b)] | | | |
|---|---|---|---|---|
| | 1-octene | cyclohexene | cyclooctene | 1-methylcyclohexene |
| TFTEP•FeCl | 1 | 4.5 | 14.7 | 15.2 |
| OEP•FeCl | 1 | 5.5 | 14.1 | 16.4 |
| TFTEP•MnCl | 1 | 7.5 | 17.1 | 29.4 |
| OEP•MnCl | 1 | 9.8 | 14.0 | 29.2 |
| TPP•FeCl[c)] | 1 | 20 | — | 84 |

a) In $CH_2Cl_2$, at 0 °C and under Ar atmosphere. [porphyrin] = $2.7 \times 10^{-4}$ mol dm$^{-3}$, [PhIO] = $2.8 \times 10^{-3}$ mol dm$^{-3}$ , [1-octene] = [other olefins] = 0.2 mol dm$^{-3}$. b) The values are determined by the product ratios. c) Ref. 6.

Based on these results, epoxidation of norbornene catalyzed by TFTEP•Fe (or Mn) was investigated using iodosobenzene as the oxygen source (Eq. 2). The reactions proceed quite normally to afford two main



(2)

Table 2. Oxidation of Norbornene Catalyzed by Porphyrin Metal Complexes[a)]

| Porphyrin | Yield / % [b)] | | | |
|---|---|---|---|---|
| | exo / endo | epoxide | aldehyde (**A**) | ketone (**B**) |
| TFTEP•FeCl | 98 | 62 | 3.9 | 0.3 |
| OEP•FeCl | 92 | 66 | 1.6 | 0.2 |
| TFTEP•MnCl | 466 | 71 | 0.8 | 0.2 |
| OEP•MnCl | 410 | 72 | 0.2 | 0.1 |
| TPP•FeCl [c)] | 55 | 54 | 3.4 | 0.4 |
| T(2-$NO_2$)PP•FeCl [c)] | 20 | 73 | 2.9 | 0.8 |
| T(2,4,6-Me)PP•FeCl [c)] | 24 | 77 | 0.4 | 0.3 |

a) In $CH_2Cl_2$, at 0 °C and under Ar atmosphere. [porphyrin] = $1 \times 10^{-4}$ mol $dm^{-3}$, [PhIO] = $6.4 \times 10^{-2}$ mol $dm^{-3}$, [norbornene] = 1 mol $dm^{-3}$. b) Based on used PhIO. c) Ref. 2b.

products, exo- and endo-norbornene oxide. Two other minor products, norcamphor (**A**) and cyclohexene-4-carboxyaldehyde (**B**), are also confirmed as previously reported.[2)] The results are summarized in Table 2 together with the data for TPP derivatives reported by Traylor. Most interesting aspect in the present results is that the exo/endo product ratio obtained for TFTEP, in spite of its strongly electron deficient character, is practically same with that for OEP and the ratio seems to be affected only by the central metal.[7)] These results are in contrast with those of TPP derivatives which show clear Hammett relationships between the exo/endo ratio and $\sigma_Y$ of substituents on phenyl rings. If one can assume that the limited electron transfer mechanism proposed for the reactions catatalyzed by TPP derivatives is also applicable for those by present flat metallo porphyrins, the data obtained here suggest that the exo/endo ratio in norbornene epoxidation catalyzed by metallo porphyrin depends not only on the electron density but also on a steric environment.[8)] Thus the exo/endo product ratios observed for OEP and TFTEP metal complexes primarily reflect a steric repulsion between the porphyrin plane and norbornene in the transition state, while those for TPP derivatives are dominated by both of steric repulsions between the porphyrin (including the meso-phenyl groups) and norbornene and the electron density of the oxene site. The importance of the steric effect in epoxydation catalyzed by TPP derivatives is also observed for tetramesitylporphyrin which shows relatively small exo/endo ratio similar to that for T(2-$NO_2$)PP in spite of rather electron donating character of methyl groups (see Table 2 and Ref. 2). These results strongly indicate that the relationship between the electronic effect and the transition state geometry in P-450 type epoxidation should be argued under condition that all porphyrin metallo complexes under discussion have similar steric environments.[9)]

Finally, it should be noted that the exo/endo ratio obtained for present highly electron deficient TFTEP•FeCl is larger than that for most electron rich TPP derivatives such as T(4-OMe)PP•FeCl (exo/endo = 86), but still much smaller than that for usual epoxidation reagent such as MCPBA (exo/endo = 690).[2b)] These interesting observations seem to indicate that the distance between TFTEP•Fe=O and norbornene in the transition state is almost the limit of the shortest transition state distance in the P-450 type epoxidation catalyzed by a porphyrin Fe complex but it still has more loose transition state compared with that for MCPBA epoxidation.

References

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5) The solvent system, $CH_2Cl_2/CF_3CH_2OH/H_2O$ (100/10/1), which gives a completely homogeneous solution of PhIO is used, see T. G. Traylor, J. C. Marsters, T. Nakano, and B. E.Dunlap, *J. Am. Chem. Soc.*, **107**, 5537 (1985). The reaction conditions ; [porphyrin]= $6.8 \times 10^{-3}$ mol $dm^{-3}$, [PhIO] = $4 \times 10^{-3}$ mol $dm^{-3}$, [cyclohexene] = 0.51 mol $dm^{-3}$, at 0 °C. The reaction is quite clean, i.e., for example, the system of TFTEP•MnCl gives cyclohexene oxide in 73% yield based on PhIO used which corresponds to 432 turnover number of the catalyst and over 80% of the original Soret band remains at this point (after 100 min).

6) J. R. Smith and P. R. Sleath, *J. Chem. Soc., Perkin Trans. 2*, **1982**, 1009.

7) The dependency of the exo/endo ratio on metal species series is accounted for by the change in transition-state geometry from limiting electron transfer processes to limiting electrophilic addition mechanism, see Ref. 2.

8) T. G. Traylor, private communication.

9) One of possible explanations consistent with these results is that two types of steric effects, steric repulsion between norbornene and the *porphyrin plane* which determines the exo/endo product ratio and steric hindrance at *meso positions* which affects the distance of M=O---norbornene, are operating independently.

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