**Table I.** Comparison of S–S Bond Lengths in Systems Containing $S_4$ Ligands

| | S(1)–S(2) | S(2)–S(3) | S(3)–S(4) | ref |
|---|---|---|---|---|
| $[Au(CH_2)_2P(C_6H_6)_2]_2S_8$ | 1.991 (13) | 1.907 (19) | 2.036 (14) | this work |
| $[Au(CH_2)_2P(C_6H_6)_2]_2S_9$ | 2.041 (29) | 2.017 (40) | 2.041 (29) | this work |
| $(Ph_3P)_2PtS_4$ | 2.024 (8) | 2.022 (10) | 2.081 (10) | 8 |
| $[AsPh_4][Mo_2S_{10}]^{(a)}$ | 2.019 (5) | 1.970 (6) | 2.115 (5) | 9 |
| $[AsPh_4][Mo_2S_{10}]^{(a)}$ | 2.096 (16) | 1.936 (19) | 2.169 (14) | 10 |
| $(Et_4N)_2MoS_4$ | 2.107 (1) | 2.012 (1) | 2.166 (1) | 11 |
| $(\mu^5\text{-}C_5H_5)_2MoS_4$ | 2.081 (8) | 2.018 (9) | 2.085 (7) | 12 |
| $(\mu^5\text{-}C_5H_5)_2WS_4$ | 2.105 (7) | 2.016 (8) | 2.116 (9) | 13 |
| $BaS_4\cdot H_2O^a$ | 2.069 (4) | 2.063 (4) | 2.069 (4) | 14 |
| $BaS_4\cdot H_2O^a$ | 2.079 (3) | 2.062 (4) | 2.079 (3) | 14 |

[a] Two or more crystallographically different $S_4$ groups per molecule.

best described as square-planar. Within each dinuclear gold(II) ylide a discrete gold–gold bond is formed. The overall configuration of the ylide units in both complexes is that of a twisted boat; other structural features of the ylide groups are unexceptional and will not be discussed further here except to note that both chair and boat configurations are typically observed in these systems.[6,7]

The geometries of the polysulfide groups in the structures described here are similar to those observed in other transition-metal–polysulfide systems. The S–S–S bond angles range from 104 (7)° to 111 (8)° and are well within the range normally observed in other transition-metal complexes containing large polysulfide ligands. The sulfur–sulfur bond distances observed in the $S_4$ linkages of both complexes show the alternation in length occasionally observed in other systems and range from 1.907 (19) to 2.036 (19) Å. The very short 1.907 (19) Å bond formed between S2 and S3 in **3** is an extreme example of this phenomenon and is, in fact, one of the shortest S–S bonds documented in the chemical literature (Table I).

The coordination behavior of the polysulfide ligands in both of these complexes is quite unusual. Only in a limited number of instances have polysulfide ligands been observed to bridge two or more transition-metal centers. Because of the large number of atoms involved in forming these heterocyclic ring systems, these adducts are the largest closed-ring metal–sulfide structures reported to date.

Of interest structurally in these complexes are the nonbonding inter- and intramolecular contacts. In the product containing four- and five-atom sulfur bridges, the intradimer metal distances measure 4.493 (8) and 4.633 (8) Å for Au1–Au1′ and Au2–Au2′, respectively. In the smaller adduct containing two four-atom sulfur bridges, the crystallographically imposed inversion center makes the corresponding distances equal at 4.457 Å. In the crystal lattice of **3** we find no particularly unusual nonbonding contacts. However, in the orthorhombic lattice of **2** we find S2 of one molecule to be only 3.2303 (3) Å away from S5 in an adjacent molecule; a distance 0.37 Å less than the sum of their van der Waal's radii.

It is interesting that the less symmetrical 13-atom complex **2** is obtained in good yield (>50%) as the principal (almost sole) product obtained by using an aqueous solution containing an equilibrium distribution of anions. In contrast, the reaction involving solid $Na_2S$ results in several as yet uncharacterized products but includes, in small yield (<5%), **3**. The reaction of $H_2S$ with the gold(II) benzoate dimer, however, does produce **3** in nearly quantitiative yield, and hydrogen has been identified in a GC analysis of the reaction. The linear S–Au–Au–S geometry in these adducts plays a role in determining the most stable ring size; however, the reasons behind the preferential formation of the 13-atom product remain unclear at this point. Because of the unusual nature of these complexes and their reactivity with $H_2S$, both their physical properties and chemical reactivities are currently being examined.

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**Registry No. 1**, 89462-50-0; **2**, 101544-50-7; **3**, 101519-30-6; **4**, 90990-50-4; $Na_2S$, 1313-82-2; $H_2S$, 7783-06-4; ammonium polysulfide, 9080-17-5; gold, 7440-57-5.

**Supplementary Material Available:** Lists of fractional atomic positional parameters, thermal parameters, bond length and angle data, hydrogen atom parameters, details of the crystallographic experimental procedures, and tables of observed and calculated structure factors amplitudes (42 pages). Ordering information is given on any current masthead page.

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## On the Rate-Determining Step in the Epoxidation of Olefins by Monooxygenase Models

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Currently, synthetic metalloporphyrins are receiving considerable interest as models of the cytochrome P-450 class of enzymes.[1] With single oxygen donors, e.g., iodosylbenzene,[1a] amine oxides,[1b] and hypochlorite,[2] these compounds form high-valent oxometal complexes (e.g., **2**), which, like the monooxygenases, are capable of oxygenating hydrocarbons. Recently, kinetic studies have appeared that deal with the mechanism of hydrocarbon oxidation by cytochrome P-450 models.[3-6] In some of these studies it was proposed that the rate-limiting step in the reaction is the formation of the high-valent oxometal complex.[3,5] In other studies, however, it was suggested that the rate-determining process is the transfer of oxygen from the oxometal complex to the substrate.[4] We wish to point out here that (i), in certain cytochrome P-450 model systems, dimerization of the active metalloporphyrin may occur and (ii) that this dimerization reaction has consequences for the kinetic analysis of the systems.[7] We will illustrate this point for the epoxidation of olefins by the monooxygenase model manganese(III) porphyrin with sodium hypochlorite as oxidant in the two-phase system water–dichloromethane (Meunier system[2]). With regard to the rate-determining step in this model, conflicting opinions exist.[4,5]

Previously, we reported that the epoxidation of cyclohexene by $Mn^{III}$(TPP)OAc and NaOCl is zero order in substrate.[5,8] Depending on the concentration of oxidant, the reaction order in hypochlorite varies between zero and one. We proposed that the rate-determining step in the catalytic process is the conversion of manganese(III) hypochlorite species **1** into the oxomanganese complex **2**.[5] This step is catalyzed by pyridine. Collman et al. recently measured the rate of epoxidation by $Mn^{III}$(TPP)Cl and LiOCl for various olefins and likewise reported that the order in

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[1] (a) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786–5791. (b) Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 6123–6125. (c) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515–3521.

[2] Meunier, B.; Guilmet, E.; De Carvalho, M. E.; Poilblac, R. *J. Am. Chem. Soc.* **1984**, *106*, 6668–6676.

[3] Powell, M. F.; Pai, E. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 3277–3285.

[4] (a) Collman, J. P.; Brauman, J. I.; Meunier, B.; Raybuck, S. A.; Kodadek, T. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 3245–3248. (b) Collman, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, Th.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000–2005. (c) Collman, J. P.; Kodadek, Th.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343–4345.

[5] (a) Razenberg, J. A. S. J.; Nolte, R. J. M.; Drenth, W. *Tetrahedron Lett.* **1984**, *25*, 789–792. (b) Razenberg, J. A. S. J.; Van der Made, A. W.; Smeets, J. W. H.; Nolte, R. J. M. *J. Mol. Catal.* **1985**, *31*, 271–287.

[6] Lindsay Smith, J. R.; Sleath, P. R. *J. Chem. Soc., Perkin Trans 2* **1982**, 1009–1015.

[7] In the enzyme, dimerization is prevented by the apoprotein. Cf.: White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315–356.

[8] Abbreviations: TPP = *meso*-tetraphenylporphyrinato; TPP = *meso*-tetra-*p*-tolylporphyrinato; TMP = *meso*-tetramesitylporphyrinato; TTMeOPP = *meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrinato; TMeOPP = *meso*-tetrakis(4-methoxyphenyl)porphyrinato; TFPP = *meso*-tetrakis(4-fluorophenyl)porphyrinato.

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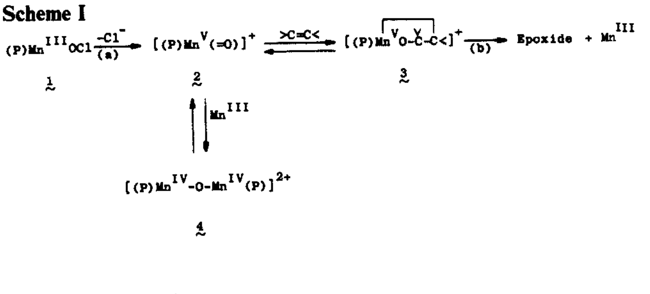
**Scheme I**



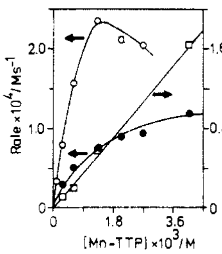


**Figure 1.** Rate of epoxidation of cyclohexene (●), 1-methylcyclohexene (○), and styrene (□) as a function of $Mn^{III}(TPP)OAc$ concentration.

olefin is zero.[4a,b] Remarkably, however, they found that various olefins epoxidize at different rates. This result, which was confirmed by us, was taken by these authors as evidence for the involvement of olefin in the rate-determining step of the reaction. This step was proposed to be the decomposition of an intermediate metallaoxetane[4a,b] (**3**) formed from olefin and the active species **2** (Scheme I, step b). The above-mentioned kinetic results, however, can equally well be explained by a mechanism in which the formation of **2** is rate-determining (Scheme I, step a) and in which the decomposition of **2** goes via two routes: one with olefin to give epoxide and a second one with manganese(III) to form an unreactive dimer **4**.[9] Olefins with a higher reactivity will have a lower stationary-state concentration of **2** and, consequently, a smaller amount of manganese complex will be present in the equilibrium **2** ⇌ **4**. In this case, more manganese in the form of complex **1** will be available for further reaction. Hence, different olefins can display different rates in spite of the fact that they do not participate directly in the rate-determining step.[10]

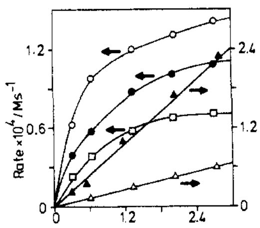


**Figure 2.** Rate of epoxidation of cyclohexene as a function of catalyst concentration: $Mn^{III}(TFPP)OAc$ (○), $Mn^{III}(TPP)OAc$ (●), $Mn^{III}(TMeOPP)OAc$ (□), $Mn^{III}(TMP)OAc$ (△), $Mn^{III}(TTMeOPP)OAc$ (▲).

We have tested this hypothesis by measuring the rate of epoxidation as a function of manganese concentration for a number of olefins and manganese(III) porphyrins having different reactivities and steric requirements.[11] Some data are given in Figures 1 and 2. For highly reactive substrates (e.g., styrene) the reaction order in manganese is one. The same result is obtained when porphyrins are used for which dimerization is not possible because of steric reasons ($Mn^{III}(TMP)OAc$ and $Mn^{III}(TTMeOP)OAc$).[8] The remaining olefins and catalysts in Figures 1 and 2, however, display curves in which the rate levels off at high manganese concentrations, suggesting that active catalyst is taken away by the equilibrium **2** ⇌ **4**.

Further evidence which supports the dimerization of the active porphyrin in synthetic model systems comes from experiments with manganese porphyrins anchored to a rigid polymer support. These experiments reveal that on anchoring, which creates site isolation, the epoxidation rate is considerably enhanced.[5b]

Finally, we found that addition of methanol (25 vol %, $MeOH/CH_2Cl_2$ ratio in the organic phase 0.10 v/v) to the reaction medium increases the rate by a factor of 3 and changes the reaction order in olefin from zero to one.[12] We verified that addition of this reagent did not change the product distribution. In the presence of methanol, the conversion of uncharged **1** to charged **2** is probably facilitated due to the higher polarity of the medium. Step a is now accelerated to such an extent that the rate-determining step of the reaction changes to (b).[13]

In conclusion, our experiments have revealed that dimerization of the metalloporphyrin may well be a complicating factor in the kinetic analysis of monooxygenase model systems.[14] Our results for the manganese porphyrins can probably be transferred to other systems, e.g., the biologically more relevant iron porphyrins. Care should therefore be taken when drawing conclusions with regard to the rate-determining step in these systems.

**Acknowledgment.** We thank professor W. Drenth for stimulating discussions.

**Registry No.** $Mn^{III}(TFPP)OAc$, 101565-34-8; $Mn^{III}(TPP)OAc$, 58356-65-3; $Mn^{III}(TMeOPP)OAc$, 101565-35-9; $Mn^{III}(TMP)OAc$, 101565-36-0; $Mn^{III}(TTMeOPP)OAc$, 98827-71-5; HClO·Na, 7681-52-9; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; styrene, 100-42-5; cytochrome P-450, 9035-51-2.

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(9) Dimeric μ-oxomanganese(IV) porphyrin complexes have been isolated and characterized by Hill et al.: Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510–3515.

(10) If we denote olefin by S, monomeric manganese porphyrin by Mn, dimeric manganese porphyrin by Dm, and the rate constants of the various steps in Scheme I as follows:

$$\mathbf{1} \xrightarrow{k_1} \mathbf{2}\ (\underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathbf{4})\ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{3} \xrightarrow{k_3} \text{epoxide}$$

we can derive the following rate equation

$$v = \frac{(k_1[\mathrm{Mn}] + k_{-4}[\mathrm{Dm}])[\mathrm{S}]}{[\mathrm{S}] + (k_{-2} + k_3)k_4[\mathrm{Mn}]/k_2k_3} \qquad (1)$$

If we make the assumption $k_{-4}[\mathrm{Dm}] \ll k_1[\mathrm{Mn}]$ and $k_{-2} \ll k_3$, (1) reduces to the more simple equation, (2). For reactive substrates or sterically hindered

$$v = \frac{k_1[\mathrm{Mn}][\mathrm{S}]}{[\mathrm{S}] + (k_4/k_2)[\mathrm{Mn}]} \qquad (2)$$

porphyrins, $k_2$ will probably be much larger than $k_4$. Since $[\mathrm{Mn}] \ll [\mathrm{S}]$ we may neglect the right term in the denominator of (2). Equation 2 now reduces to $v = k_1[\mathrm{Mn}]$. The epoxidation reaction is independent of substrate concentration and its rate is determined by $k_1$ exclusively. In the reverse case, i.e., relatively unreactive substrates or sterically nonhindered porphyrins, the condition $(k_4/k_2)[\mathrm{Mn}] \gg [\mathrm{S}]$ could hold. Equation 2 reduces to $v = (k_1k_2/k_4)[\mathrm{S}]$. The epoxidation reaction is now independent of manganese concentration and first order in substrate concentration. Experimentally, we found that for solutions containing, e.g., 0.8 M cyclohexene and 0.008 M $Mn^{III}(TPP)OAc$, deviation from zero-order behavior occurs after ≃50% of olefin had been converted. For lower catalyst concentrations ($Mn^{III}(TPP)OAc$ < 0.003 M) reactions remain zero order in substrate concentration up to 80% conversion. A generalized kinetic analysis without the assumptions mentioned above will be given in a full paper. In the limiting cases, however, similar conclusions are reached.

(11) In a typical experiment, the following components were mixed: olefinic substrate (0.480 mmol), toluene (internal standard, 0.105 mmol), $Mn^{III}(TPP)OAc$ ($1.72 \times 10^{-3}$ mmol), 4-methylpyridine (0.670 mmol), and benzyltriethylammonium chloride ($2.8 \times 10^{-3}$ mmol) in $CH_2Cl_2$ (0.5 mL). To this solution an aqueous solution of NaOCl (2 mL, 0.35 M, pH 13) was added. From time to time samples (1 μL) were taken which were analyzed by GLC (carbowax 20 M on Chromosorb W-HP). We verified that under our conditions the catalyst was not starved of oxidant.

(12) Razenberg, J. A. S. J.; Nolte, R. J. M.; Drenth, W. *J. Chem. Soc., Chem. Commun.*, in press.

(13) Kinetic data (details to be published in a full paper) suggest that complex **2** reacts with olefin to give an intermediate, whose structure is not fully understood yet. This intermediate could either be a metallooxetane (**3**), a carbocation [$Mn^{III}$(O-C<C<$^+$)], or a radical [$Mn^{IV}$(O-C<C<·)].

(14) The experiments in the literature (see ref 4) were conducted under somewhat different reaction conditions, i.e., using low catalyst concentration, LiOCl as oxidant, and an imidazole instead of pyridine. Under these conditions it could be possible that the rate-determining step is shifted to step b (Scheme I). Therefore, our results and those found in the literature may not necessarily be contradictory but can be interpreted to mean that the rate-determining step of the catalytic cycle depends on the reaction conditions employed.