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The Novel Formation of Metalloporphyrin-Oxo Species in Singlet Oxygen Oxidation of Adamantylideneadamantane

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Oxygen-containing complexes of some metalloporphyrins related to cytochrome P-450 have recently become the subject of great interest and intensitve investigation.[1] A variety of chemical oxidants such as peracids,[2] alkyl hydroperoxides,[3] iodosylbenzene (PhIO),[4] hypochlorite,[5] and a persulfoxide intermediate generated in singlet oxygen ($^1O_2$) oxidation of sulfide[6] have been used as oxygen donors to form the metal–oxo species (M=O); on the other hand, O_2 has been an oxygen atom source by modeling of the reductive dioxygen activation.[7] Meanwhile, it is well known that $^1O_2$ oxidation of olefin results in the formation of allylic hydroperoxide via a perepoxide intermediate.[8] In $^1O_2$ oxidation of adamantylideneadamantane (Ad=Ad), affording the corresponding dioxetane in high yield,[9] a perepoxide intermediate was trapped by sulfoxide,[10] sulfur dioxide,[11] and phosphite[12] to give sulfone, sulfur trioxide, and phosphate, respectively. To our knowledge, no interaction between a perepoxide and a metal ion, however, has been known. We describe here a novel oxygen-transfer system from $^1O_2$ to a hydrocarbon via perepoxide and metal–oxo species intermediates owing to the catalytic role of the porphyrin–metal complex.

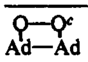
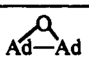
In a typical experiment, a benzene solution of Ad=Ad (1.9×10^{-2} M) and adamantane (17 equiv) was photoirradiated at 20 °C with tetraphenylporphin (TPP, 3.5×10^{-4} M) as sensitizer under an oxygen flow (flow rate; 2 mL/min) in the presence of Mn(TPP)Cl (3.2×10^{-4} M).[13] The resulting mixture was submitted to analytical GLC and GC-MS. Both adamantan-1-ol and adamantan-2-ol were apparently produced in 62% and 17% yields, respectively, together with adamantylideneadamantane oxide (84%) and dioxetane (11%) (Table I, run 1). All yields were based on Ad=Ad consumed. Very similar results were also obtained with cyclohexane (Table I, runs 2, 4, 6). Control reactions reveal that all of the components, Ad=Ad, $^1O_2$,[14] and metal porphyrin, are essential for hydroxylation. No degradation of the catalyst was observed. An oxygen acceptor such as cyclohexane, adamantane, or norbornene is inert toward singlet oxygen. The results are summarized in Table I.

Both PhIO/Mn(TPP)Cl[13] and our Ad=Ad/$^1O_2$/Mn(TPP)Cl system give similar kinetic isotope effects in the hydroxylation of a mixture of cyclohexane-d_{12} and cyclohexane ($k_H/k_D = 8.8$ and 8.6, respectively). These observations suggest the intermediacy of the same metal–oxo species (Mn=O(TPP)Cl).

In order to know the character of the active oxidizing species, the steric effects of both an added olefin and a catalyst have been investigated. Mn=O(TPP)Cl has a stronger ability for hydroxylation compared with Fe=O(TPP)Cl (Table I, runs 1–4, 10, 11).[16,17] Moreover, Table I (runs 10,11) reveals that norbornene as a less sterically hindered olefin is more easily oxidized to epoxide compared with Ad=Ad.[16] Compared with the PhIO system, a large steric effect was observed for epoxidation of norbornene using a series of iron porphyrins with sterically protected pockets in the Ad=Ad/$^1O_2$ system. The observed selectivity depends on the size of the substituents on the porphyrin ring (Table II).[5a] These results with the sterically crowded Ad=Ad perepoxide intermediate suggest that the slow step in the mechanism is the formation of the metal–oxo species.

Thianthrene 5-oxide was used as a useful chemical monitor for clarifying the electrophilic character of the oxygen-transfer agent.[6a,18] The perepoxide intermediate derived from the $^1O_2$ oxidation of Ad=Ad acted completely as a nucleophile ($X_{Nu} \approx 1$)(Table III, run 1).[10,12] As expected, the metal–oxo species M=O(TPP)Cl derived from the M(TPP)Cl/PhIO system gave an essentially electrophilic attack (X_{Nu} 0.42–0.53)(Table III, runs 2–4).[1,7] In the $^1O_2$ oxidation of Ad=Ad in the presence of M(TPP)Cl, a less nucleophilic oxygen-transfer reaction occurred toward thianthrene 5-oxide (X_{Nu} 0.88–0.96)(Table III, runs 5–7). These results apparently suggest that the oxidant, together with the nucleophilic perepoxide intermediate, produced in the $^1O_2$

Table I. Oxidation of Alkanes with Perepoxide or PhIO Catalyzed by Metal Tetraphenylporphyrin

			products, yield[b] (%)							
run	oxidation system[a]	substrate	 Ad–Ad (dioxetane)[c]	 Ad–Ad (epoxide)	Ad=Ad–OH[d]	1-AD-OH	2-Ad-OH	2-Ad=OO	cyclohexanol	catalyst[e] turnover
1	Ad=Ad/$^1O_2$/ Mn(TPP)Cl	adamantane	11	84	trace	62	17	–[f]		23
2		cyclohexane	35	65					40	13
3	Ad=Ad/$^1O_2$/ Fe(TPP)Cl	adamantane	26	72	trace	38	5	–[f]		12
4		cyclohexane	9	84					11	3
5	Ad=Ad/$^1O_2$	adamantane	94	6		nd[g]	nd	–[f]		
6		cyclohexane	95	5					nd	
7	$^1O_2$/Mn(TPP)Cl	adamantane				nd	nd	nd		
8	olefin[h]/$^1O_2$/ Mn(TPP)Cl	adamantane	12	88		58	15	10		21(24[i])
9	PhIO/ Mn(TPP)Cl[j]	adamantane				56[k]	17[k]	9[k]		18(20[i])
10	PhIO/ Mn(TPP)Cl[l]	Ad=Ad/ norbornene		1	8[m]	*exo*-norbornene oxide		57[n]		
11	PhIO/ Fe(TPP)Cl[l]	Ad=Ad/ norbornene		2	3[m]	*exo*-norbornene oxide		14[n]		

[a] The reaction conditions were as follows: adamantane/olefin/metalloporphyrin = 1000/60/1 in benzene, [metalloporphyrin) = 3.2×10^{-4} M; cyclohexane/olefin/metalloporphyrin = 6000/60/1 in benzene, [metalloporphyrin] = 6.4×10^{-4} M. [b] Yields were based on Ad=Ad consumed. 50% of Ad=Ad was converted in all cases. [c] In the presence of metalloporphyrin, dioxetane did not decompose under the experimental conditions. [d] Adamantylideneadamantan-4-ol. [e] Alcohols produced/porphyrin used. [f] Since the dioxetane was decomposed under GC analysis, yield of adamantan-2-one was not determined. [g] Not detected. [h] Biscyclo[3.3.1]nonylidenebiscyclo[3.3.1]nonane. [i] Alcohols and ketone produced/porphyrin used. [j] Adamantane/PhIO/metalloporphyrin = 1000/25/1 in benzene. [k] Yields were based on PhIO consumed. [l] The reaction conditions were as follows: norbornene/Ad=Ad/PhIO/metalloporphyrin = 30/30/10/1 in CH_2Cl_2, [metalloporphyrin] = 1.4×10^{-3} M. [m] Other possible products were the hydroxylated Ad=Ad. [n] Traces of the *endo*-epoxide, norcamphor, and 3-cyclohexene-1-carboxaldehyde were also detected.

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Table II. Relative Rates of Catalytic Epoxidation of Norbornene Using Iron Porphyrin

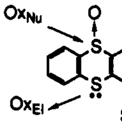
	Iron Porphyrin		
oxidation system	Fe(TMP)Cl	Fe(TPP)Cl	Fe(OEP)Cl
Ad=Ad/$^1O_2$[a]	0.57[b]	1.0[b]	3.0[b]
PhIO[c]	0.83[b]	1.0[b]	0.77[b]

[a] The reaction conditions were as follows: norbornene/Ad=Ad/metalloporphyrin = 7000/60/1 in CH_2Cl_2, [metalloporphyrin] = 6×10^{-4} M, [TPP] = 3.5×10^{-4} M. [b] Relative rates were calculated on the basis of the yields of norbornene oxide produced at the stage of 50% conversion of Ad=Ad. [c] Norbornene/PhIO/metalloporphyrin = 7000/30/1, [metalloporphyrin] = 6×10^{-4} M. [d] Relative rates were calculated on the basis of the yields of norbornene oxide produced at the complete consumption of PhIO.

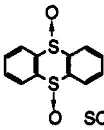
Table III. Nucleophilic Character (X_{Nu}) of Oxygen-Transfer Agents Derived with Thianthrene 5-Oxide

			abs yield (mM)[b]			
run	oxygen-transfer reactions[a]	total yields (%)	SSO_2, n_{Nu}	SOSO, n_{El}	$SOSO_2$, n_{Nu}, n_{El}	X_{Nu}[c]
1	Ad=Ad/$^1O_2$/CH_2Cl_2/20 °C	3.7	3.53			1.00
2	Fe(TPP)Cl/Ad=Ad/$^1O_2$/CH_2Cl_2/20 °C	2.6	2.37	0.11	trace	0.96
3	Fe(TPFP)Cl/Ad=Ad/$^1O_2$/CH_2Cl_2/20 °C	2.5	2.05	0.20	0.09	0.88
4	Mn(TPP)Cl/Ad=Ad/$^1O_2$/CH_2Cl_2/20 °C	9.0	7.43	0.54	0.54	0.88
5	Mn(TPP)Cl/PhIO/CH_2Cl_2/20 °C	15.3	8.95	3.36	2.22	0.53
6	Fe(TPP)Cl/PhIO/CH_2Cl_2/20 °C	9.7	2.88	4.36	1.97	0.43
7	Fe(TPFP)Cl/PhIO/CH_2Cl_2/20 °C	13.9	3.53	6.17	3.44	0.42

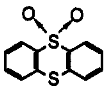
[a] A trace of oxidized products of thianthrene 5-oxide was obtained in PhIO/CH_2Cl_2/20 °C, $^1O_2$/CH_2Cl_2/20 °C, and Fe(TPFP)Cl/$^1O_2$/CH_2Cl_2/20 °C systems. [b] The typical ratio of reactants, thianthrene 5-oxide/Ad=Ad/PhIO/porphyrin, is 80/30/20/1, [porphyrin] = 1.2×10^{-4}. Amount of conversion of thianthrene 5-oxide into SSO_2, SOSO, and $SOSO_2$ products determined by GLC. [c] Mole fraction of amount of nucleophilic attack, i.e., $n_{Nu}/(n_{Nu} + n_{El})$; $SOSO_2$ represents double oxygen-transfer product either via the sequence $\mathrm{SSO} \xrightarrow{\mathrm{Ox_{El}}} \mathrm{SOSO} \xrightarrow{\mathrm{Ox_{Nu}}} \mathrm{SOSO_2}$ or $\mathrm{SSO} \xrightarrow{\mathrm{Ox_{Nu}}} \mathrm{SSO} \xrightarrow{\mathrm{Ox_{El}}} \mathrm{SOSO_2}$, so that the yield of $SOSO_2$ is equally added to n_{Nu} and to n_{El}.



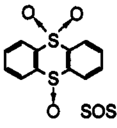
SSO



SOSO(EI)

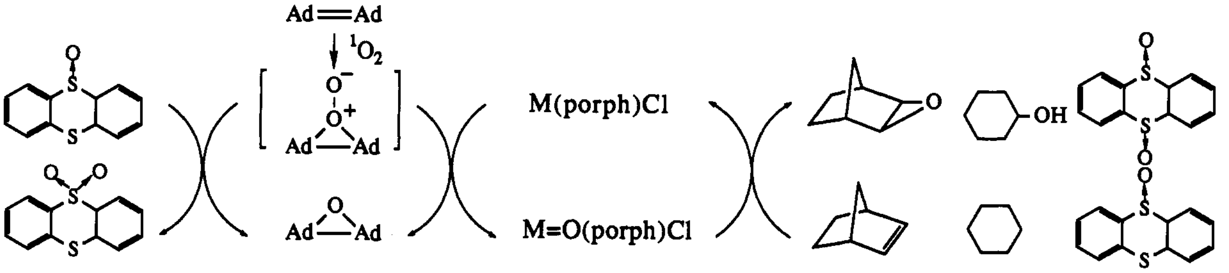


SSO_2(Nu)



$SOSO_2$(EI, Nu)

Scheme I



oxidation of Ad=Ad in the presence of M(TPP)Cl should have an essentially electrophilic character.

On the basis of these observations, the primary perepoxide intermediate is likely to transfer an outer oxygen atom to M(porph)Cl to afford M=O(porph)Cl, which can oxidize hydrocarbon, olefin, and sulfide to alcohol, epoxide, and sulfoxide (Scheme I), respectively.

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