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Oxygen atom transfer from carbonyl oxide to alkane catalyzed by metalloporphyrin

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ABSTRACT

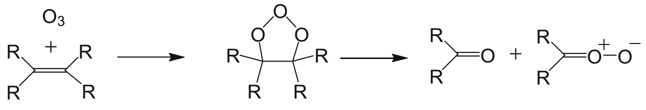
The reaction of singlet oxygen with diazofluorene in the presence of metalloporphyrin caused oxidation of hydrocarbons as well as sulfide and anisol in substantial yields. The active oxidizing species is probably a high valency metal oxo species(M=O(porph)Cl) generated by an oxygen transfer from carbonyl oxide intermediate to M(porph)Cl.

We present here evidence for oxygen atom transfer from carbonyl oxide to alkane as well as to sulfide and anisole catalyzed by manganese or iron porphyrin. Carbonyl oxides are key intermediates in ozonolysis of alkenes[1] (Scheme 1) and their reactivities have been attracting attention from biological, atmospheric, and chemical viewpoints.

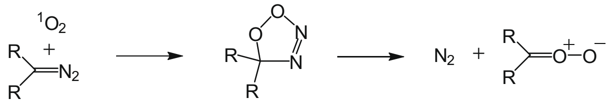
The fundamental features of carbonyl oxides are fairly well understood, as summarized in the comprehensive reviews published during 1990s.[2] On the other hand, formation of ozone in biology has been suggested in very recent studies.[3] Antibodies can catalyze the generation of ozone from singlet oxygen ($^1O_2$) and water. In spite of this new discovery in immune system, further studies of the ozone reaction with various substrates may be disturbed by not only high reactivity and short lifetime of ozone, but also by the overlapping of the ozone signal with those of other generated molecules such as H_2O_2 in spectroscopic measurement. In this context, we have used a well-known method to generate carbonyl oxide by oxidation of diazo compound with $^1O_2$ (Scheme 2).

We report here for the first time the oxygen atom transfer of carbonyl oxide as one of the ozonolysis compounds in biological system to metalloporphyrin as catalytic and biological model compound. In our previous studies, metalloporpyrins have a strong affinity for the intermediate peroxides such as persulfoxide[4] and perepoxide[5] to afford the metal-oxo species (M=O), which is thought to be involved in the model systems of cytochrome P-450 employing iron(III) porphyrin[6] and conventional chemical oxidants such as iodosylbenzene (PhIO),[7] peracids,[8] and hydroperoxide.[9]

In a typical experiment, a benzene solution of 9-diazofluorene (3.7×10^{-2} M) and cyclohexane (100 equiv) was photoirradiated at 15 °C with tetraphenylporphin (TPP, 7.0×10^{-4} M) as sensitizer, and biphenyl (1.1×10^{-2} M) as internal standard under an oxygen flow (flow rate; 2 mL/min) in the presence of Mn(TPP)Cl (1.4×10^{-3} M).[10] The resulting mixture was submitted to analytical gas chromatography and gas chromatography—mass spectroscopy (GC–MS). Cyclohexanol was apparently produced in 52% yield, together with fluorenone (Table 1, entry 1). All yields were based on 9-diazofluorene consumed. Very similar results were also obtained with adamantane. 1-Adamantanol and 2-adamantanol were produced in 35% and 6.4% yields, respectively, together with fluorenone (Table 1, entry 2). Control reactions reveal that all the components, 9-diazofluorene, $^1O_2$,[11] and metalloporphyrin, are essential for



Scheme 1. Alkene ozonolysis.



Scheme 2. $^1O_2$ oxidation of diazo compound.

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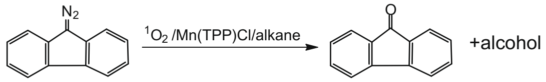
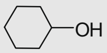
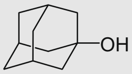
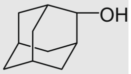
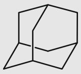
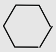
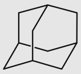
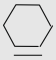
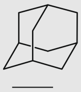
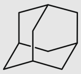
Table 1
Hydroxylation by diazofluorene/$^1O_2$/Mn(TPP)Cl system



Entry	Reaction conditions[a]	Alkane (equiv)	Diazo conv. (%)	Products, % yields[b]		
						
1	Diazo/$^1O_2$/Mn	 100	76	52	–	–
2	Diazo/$^1O_2$/Mn	 17	76	–	35	6.4
3	Diazo/$^1O_2$/–	 100	85	0	–	–
4	Diazo/$^1O_2$/–	 17	97	–	0	0
5	–/$^1O_2$/Mn		–	0	–	–
6	–/$^1O_2$/Mn		–	–	0	0
7	Diazo/O_2/Mn (dark)	 17	14	–	0	0

[a] The ratio of reactants was as follows: cyclohexane/diazofluorene/Mn(TPP)Cl (1.4×10^{-3} M) = 3000/30/1, and adamantane/diazofluorene/Mn(TPP)Cl (7.1×10^{-4} M) = 500/30/1 in benzene (1 ml).

[b] Yields are based on 9-diazofluorenone consumed. The reason why the conversion of the diazo compound as a sacrificial reagent is higher than the total yield of oxidized products of alkane, is seemed to be self-degradation of 9-diazofluorenone.

hydroxylation. No degradation of the catalyst was observed. An oxygen acceptor such as cyclohexane or adamantane is inert toward $^1O_2$ and/or the carbonyl oxide. The photooxygenation of 9-diazofluorene in the absence of metalloporphyrin gave the fluorenone quantitatively while no hydroxylation of cyclohexane or adamantane took place (Table 1, entries 3 and 4). The results are summarized in Table 1.

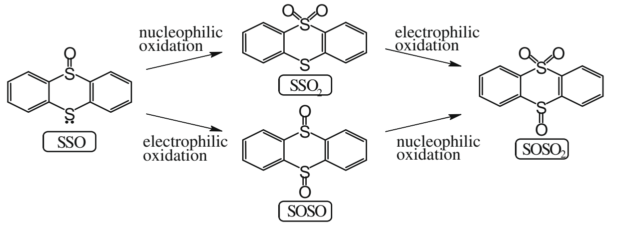
Both PhIO/Mn(TPP)Cl and the present 9-diazofluorene/$^1O_2$/Mn(TPP)Cl systems have shown similar kinetic isotope effects in the hydroxylation of a mixture of cyclohexane and cyclohexane-d_{12} (k_H/k_D = 8.8 and 8.4, respectively). These observations may clarify the intermediacy of the same metal-oxo species (Mn═O(TPP)Cl).

Moreover, (tetrakispentafluorophenylporphynato)iron chloride, Fe(TPFP)Cl, known as one of the most electronegative metalloporphyrins, has catalyzed the oxygen transfer from the carbonyl oxide intermediate to anisole-4-D to afford *p*-methoxyphenol.[12] GC–MS analysis of the resulting *p*-methoxyphenol showed 80% content of deuterium, that is, 80% of the NIH shift.[13] The marked NIH shift, similar to 60% and 72% NIH shift observed with microsomes[14] and Fe(TPFP)Cl/PhIO systems,[12] respectively, and dissimilar to Fenton's reagent (<5% NIH Shift),[15] may confirm the intermediacy of Fe^{IV}═O(TPFP)$^{+\cdot}Cl^-$ in the system.

Thianthrene 5-oxide can be used as a useful chemical monitor for clarifying the character as the oxygen-transfer agent.[2d,4,5,16] The carbonyl oxide intermediate derived from the $^1O_2$ oxidation of 9-diazofluorene acted as a nucleophile ($X_{Nu} \sim 0.85$) (Table 2, entry 1). As expected, the metal-oxo species Fe═O(TPFP)Cl derived from the Fe(TPFP)Cl/PhIO system showed an essentially electrophilic character ($X_{Nu} \sim 0.42$) (Table 2, entry 3). In the $^1O_2$ oxidation of 9-diazofluorene in the presence of Fe(TPFP)Cl, a less nucleophilic oxygen-transfer reaction occurred toward thianthrene 5-oxide ($X_{Nu} \sim 0.57$) (Table 2, entry 2). These results apparently reveal that the oxidant produced in the $^1O_2$ oxidation of 9-diazofluorene in the presence of Fe(TPFP)Cl showed an essentially electrophilic character together with the nucleophilic carbonyl oxide intermediate. This suggests the intermediacy of Fe^{IV}═O(TPFP)$^{+\cdot}Cl^-$ in the system.

In conclusion, on the basis of these observations, the primary carbonyl oxide intermediate is likely to transfer an outer oxygen atom[17]

Table 2
Nucleophilic character (X_{Nu}) of oxygen-transfer agents derived from thianthrene 5-oxide



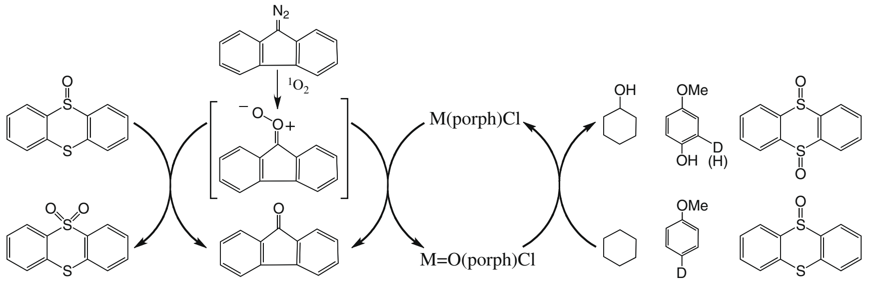
$$X_{Nu} = \frac{\text{nucleophilic oxidation}}{\text{total oxidation}} = \frac{SSO_2 + SOSO_2}{SSO_2 + SOSO + 2SOSO_2}$$

Entry	Oxygen-transfer reactions[a]	Active oxidant	Total yields %	Abs yields, mM[b]			X_{Nu}[c]	Ref.
				SSO_2 n_{Nu}	SOSO n_{El}	$SOSO_2$ n_{Nu}, n_{El}		
1	9-Diazofluorene/$^1O_2/CH_2Cl_2$; 20 °C	$[R_2C{=}O^+{-}O^-]$	15.1	11.89	0.08	2.36	0.85	This work
2	Fe(TPFP)Cl/9-diazofluorene/$^1O_2/CH_2Cl_2$; 20 °C	$[M{=}O(porph)Cl]+[R_2C{=}O^+{-}O^-]$	2.7	1.48	1.11	trace	0.57	This work
3	Fe(TPFP)Cl/PhIO/CH_2Cl_2; 20 °C	$[M{=}O(porph)Cl]$	13.9	3.53	6.17	3.44	0.42	5
4	O_3/CH_2Cl_2; −78 °C → 20 °C		3.08	3.86	19.6	0.156	0.17	15

[a] A trace of oxidized products of thianthrene 5-oxide was obtained in Fe(TPFP)Cl/$^1O_2/CH_2Cl_2$; 20 °C, $^1O_2/CH_2Cl_2$; 20 °C, and PhIO/CH_2Cl_2; 20 °C systems.

[b] The typical ratio of reactants, thianthrene 5-oxide/9-diazofluorene/PhIO/Fe(TPFP)Cl, is 80/30/20/1, [Fe(TPFP)Cl] = 1.2×10^{-3} M. 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, that is, $n_{Nu}/(n_{Nu} + n_{El})$; $SOSO_2$ represents double oxygen-transfer product either via the sequence $SSO(O_{X_{El}}) \rightarrow SOSO(O_{X_{Nu}}) \rightarrow SOSO_2$ or via the sequence $SSO(O_{X_{Nu}}) \rightarrow SSO_2(O_{X_{El}}) \rightarrow SOSO_2$, so that the yield of $SOSO_2$ is equally added to n_{Nu} and to n_{El}.



Scheme 3.

to M(porph)Cl to afford M=O(porph)Cl, which can oxidize hydrocarbon, sulfide, and anisole to alcohol, sulfoxide, and methoxyphenol, respectively (Scheme 3). The present findings may be of great help in understanding the reaction of olefin and ozone as an oxidant in synthetic application and the biological system.

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10. In the case of using Fe porphyrins instead of Mn porphyrin, similar catalytic effects were obtained in our previous study. Mn porphyrins are slightly more effective for hydroxylation, on the contrary less effective for epoxidation. The details will be reported elsewhere.
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17. In this system, carbonyl oxide (open form) and dioxirane (cyclic form) can be generated. In our case we consider that the open form is major because of high X_{Nu} (0.85) in control experiment.