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SYNERGETIC COMBINATION OF CATALYSIS OF THE PHASE TRANSFER-ELECTRON TRANSFER TYPE FOR THE OXIDATION OF ALCOHOLS OR HYDROCARBONS

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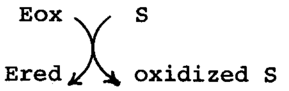
Successful synergetic combination of the electron-transfer catalyst, TPPMn, and the phase-transfer catalyst, TOMA, in the oxidation of alcohols or hydrocarbons were reported.

We have already reported that ethers or alcohols were very readily (within a few minutes at room temperature) oxidized by a pontential oxidizing reagent, hematoporphyrin·Mn(IV) complex[1,2] (abbreviated as Hm·Mn(IV)), which also decomposed water in the neutral condition as a possible model of the plant photosystem II.[3,4] Since many oxidation reactions of organic compounds with inorganic oxidants, just like many other substitution reactions with inorganic reagents, were effectively catalyzed by a phase transfer reagent,[5] it is quite reasonable to assume that the Mn·porphyrin catalyzed oxidations mentioned above may be further catalyzed by an appropriate phase transfer reagent. In this article, the authors wish to report that the electron transfer type catalyst, TPP·Mn(III) (abbreviation of meso-tetraphenylporphyrin), acts synergetically with a common phase transfer catalyst, trioctylmethylammonium salt (abbreviated as TOMA) to promote the oxidation of benzyl alcohol or many other organic substrates.

Benzyl alcohol was stoichiometrically and instantaneously oxidized with TPP·Mn(IV) at room temperature in common organic solvents (equation 1)[1] and the resultant TPP·Mn(III) was readily re-oxidized with NaOCl at room temperature in aqueous alkaline solution above pH 12 (equation 2).[1] The direct oxidation of benzyl alcohol with NaOCl (equation 3) was very slow. The direct oxidation was considerably accelerated by a phase transfer catalyst, TOMA, (equation 4) or by



homogeneous, fast

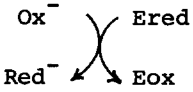
Eox = TPP·Mn(IV)

1 Ered = TPP·Mn(III)

a S = $PhCH_2OH$

oxidized S = PhCHO

b S = $PhCH_2OCH_2Ph$

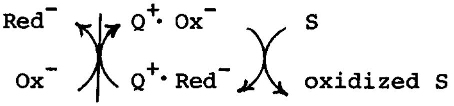


homogeneous, fast

2 $Ox^- = ClO^-$

$Red^- = Cl^-$

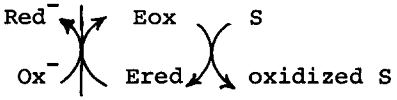
3 heterogeneous, slow



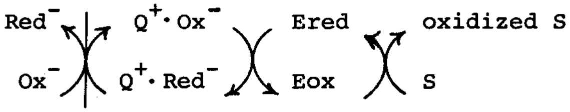
heterogeneous, catalytic,

4 moderately slow

$Q^+ = (n\text{-octyl})_3NMe^+$



5 heterogeneous, catalytic, moderately slow



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an electron transfer catalyst, TPP·Mn (equation 5) as is seen in Figure 1 or Table 1 under catalytic condition where a substrate and an oxidant (NaOCl) were used in large excess amounts over the electron transfer reagent or the phase transfer reagent.

However, these systems still involve the relatively slow interphase reaction as in **3** and **5** or the relatively slow OCl^--substrate reaction as in **3** and **4** under the catalytic condition. In the presence of both of an electron transfer catalyst (TPP·Mn) and a phase transfer catalyst (TOMA) (equation 6) the phase transfer reaction as well as the electron transfer reaction were accelerated to a reasonable extent and the overall oxidation became extremely fast (within a few minutes) as shown in Table 2. This is the interesting example where combination of two independent and very effective catalysts affords a remarkable synergetic effect.

Table 1. Product of the Synergetic Catalysis, Hypohalite Oxidation^a

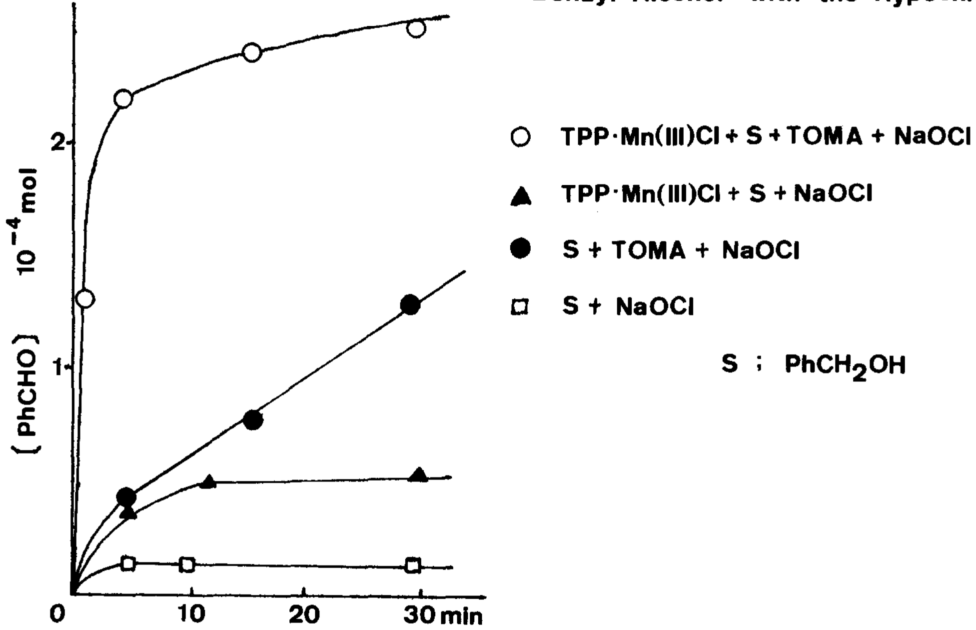
substrate	reaction time (min)	oxidation product and yield (%)^b			
øCH$_2$OH	1.5	øCHO	88 (125)		
	5	øCHO	94 (150)		
	60^c	øCHO	57 (1771)	øCOOH	9 (290)
(øCH$_2$)$_2$O	1	øCHO	85 (189)		
øCH$_2$Oi-Pr	1	øCHO	79 (232)		
RH$_2$^{d}	20	RHCl	76 (1100)	R=O	4 (55)

a) TPP·Mn(III)Cl (7.2×10^{-5}mol), TOMA (1.2×10^{-4}mol), substrate (ca.2×10^{-3} mol) and NaOCl (3.6×10^{-4}mol) in CH_2Cl_2–H_2O (3 ml / 2 ml). b) Based on substrate consumed, the value in parenthesis was based on TPP·Mn(III)Cl used.

c) Further NaOCl (3.6×10^{-4}mol) was added after 20 and 30 min.

d) Cyclohexane.

Fig 1 The Time-Conversion of the Catalytic Oxidation of Benzyl Alcohol with the Hypochlorite



Very interesting to note is that the present oxidation system is also applicable to unsubstituted saturate hydrocarbons. Adamantane (abbreviated as Ad-H, 1.5 mmol), for example, together with TPP·Mn(III)Cl (0.07 mmol) and TOMA·Cl$^-$ (0.12

mmol) was dissolved in 3 ml of methylene chloride and the solution was shaken (190 cycle/min) with a 2 ml of alkaline NaOCl (0.18 N) solution. After 200 min, usual work up gave 0.30 mmol of the product, the composition of which was: 1-AdCl 47 %, 1-AdOH 17 %, 2-AdCl 21 %, 2-AdOH 11 %, and 2-Ad=O 4 %. This regioselectivity observed, bridgehead to bridge hydrogen, was 5.3 after statistical correction, demonstrates that the most probable mechanism involved is the free radical hydrogen abstraction.[6] The finding that the addition of a typical radical scavenger, 2,6-di-t-butyl-p-cresol, inhibited the oxidation completely also supports the free radical mechanism.

Table 2. Rate Constants of Phase Transfer and Electron Transfer Catalysis[a]

oxidant	$\Delta(\phi CHO)/\Delta t(x10^{3})$	rate constant
NaOCl	1.5 min^{-1} M	k_2 = 0.0083 $min^{-1}M^{-1}$
NaOCl + TOMA·Cl	4.5	k_3 = 0.930 $min^{-1}M^{-2}$
NaOCl + TPP·Mn(III)·Cl	4.4	k_3 = 1.460 $min^{-1}M^{-2}$
NaOCl + TOMA·Cl + TPP·Mn(III)·Cl	65	k_4 = 375 $min^{-1}M^{-3}$

a) $[NaOCl]_0=3.6x10^{-4}$mol in a mixture of 3 ml of CH_2Cl_2 and 2 ml of aqueous alkaline (pH 12.8).

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