CHAPTER 4
Photo-assisted Reaction

There have been some studies earlier on the effect of light on the oxidation of hydrocarbons. Manganese, molybdenum and niobium porphyrins have been used with molecular oxygen for photocatalytic epoxidation of alkenes [1-4]. These and other epoxidations involving titanium and vanadium are slow in nature, the activity is poor and the reaction mechanism is different from the 'oxygen rebound' mechanism. Photooxidation of cycloalkanes have been reported with iron halogenated porphyrin complexes like Fe(III)(Por)(OH) under irradiation [5]. In this case, epoxide is not formed from alkene and the proposed mechanism for oxygenation of alkanes involves $^{\cdot}OH$ radical generated by photoactivation of iron hydroxoporphyrin catalyst No report appears to have been made about the effect of light on the epoxidation involving metal complex catalysts and iodosylbenzene as oxidant In the epoxidation reactions involving iodosylbenzene, it has been suggested, as discussed in chapter 1, that the reaction gets terminated due to the formation of stable μ-oxo compound.

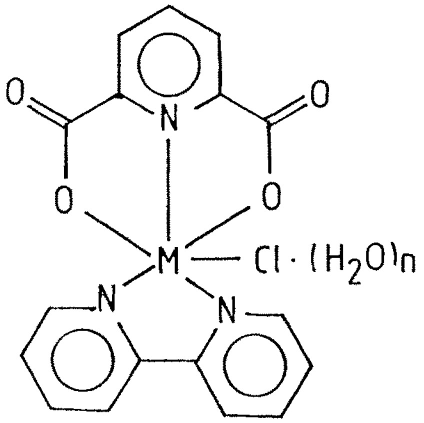
Richman et al [6] reported an interesting catalytic system comprising of μ-oxo-bis-(tetraphenylporphyrin)iron(III), which on continuous or flash photolysis disproportionates to generate the ferrous complex and the ferryl Fe(TPP)(O).

$$(TPP)Fe^{III}\text{--}O\text{--}Fe^{III}(TPP) \xrightarrow{h\nu} Fe^{II}(TPP) + (TPP)Fe^{IV}(O)$$

The latter is an active oxidizing agent and gives epoxide with alkenes. It was, therefore, thought of interest to study the oxidation of alkenes catalyzed by metal complexes in presence of light.

Experimental

Procedure followed for the study of epoxidation reactions is same as in previous chapters, except that the reactions were carried out in both dark and light. The photo-reactions were carried out in a double walled Schlenk tube of 10 ml capacity. A High Pressure Mercury Vapour (HPMV) lamp was used as light source The reaction mixture for catalytic studies was stirred magnetically and cooled by water circulation The catalytic runs were carried out under nitrogen atmosphere. Gas chromatographic analyses were done on a Shimadzu GC-14B equipped with Oracle 3 computing integrator, using FID, 10% SE-30 with 1% QF on Chromosorb W column (2 M) and nitrogen was used as carrier gas Reaction medium for epoxidation studies was acetonitrile - water solvent mixture or dioxane - water solvent mixture. Chlorobenzene was used as GC internal standard



M = Fe, n=1 **1**
= Cr , n= 0 **2**

Results and Discussion

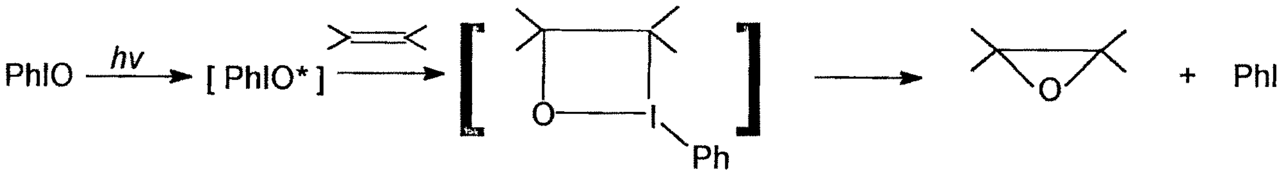
Irradiation of *cis*-cyclooctene in the solvent mixtures acetonitrile-water and dioxane-water does not show any additional peak in the GC analysis showing that the light has no effect on alkene in the absence of the catalyst and the oxidant. The results of the epoxidation reactions carried out in both the solvent mixtures, using complexes 1 and 2 with iodosylbenzene, in presence and absence of light are recorded in Table 1. Epoxide was the only product detected by the GC analysis

As observed in the earlier study (chapter 3) carried out in acetonitrile-water solvent mixture, in the present study in dioxane-water solvent mixture also, complex 1 does not act as an epoxidation catalyst. Thus complex 1 is inactive in both the solvent mixtures (Table 1, entries 1 and 2). The complex 2 shows comparable epoxidation activity in both the reaction media (entries 3 and 4) Clearly, the change of solvent does not have much effect on the catalytic activity in dark

Effect of light on the epoxidation reaction is clearly seen from entries 5 to 8, which show significant increase in the epoxide yields. Though complex 1 is catalytically inactive in dark and there is no formation of epoxide, there is epoxidation in presence of light It is also seen that though the complex 2 is catalytically active in the absence of light, the epoxidation activity is much more pronounced in the presence of light. The epoxidation activity shown by 1 on irradiation is the same as the increase in the activity of 2 on irradiation. It is also seen that change of solvent does not seem to affect the reaction in the presence of light also.

To evaluate the effect of light, control experiments, in the absence of catalyst, but in presence of light, were carried out. Entries 9 and 10 in Table 1 for these experiments show epoxide formation even in the absence of the metal catalysts. Further, the extent of epoxide formation is same as the 'excess' of epoxide formed on carrying out the catalytic reaction in the presence of metal catalysts and light compared to epoxide formed in presence of metal catalyst and absence of light. This means that the increase in the epoxide yield due to light remains the same irrespective of the presence of metal catalysts. This indicates that light independently acts as catalyst to promote the epoxidation of cis-cyclooctene by iodosylbenzene. The increase in the epoxide yield in presence of light is not because of light assisting the normal metal-oxo mediated epoxidation

This prompted us to look for alternative explanation for the catalytic role of light. Following tentative reaction pathway for the light catalyzed epoxidation of alkene with iodosylbenzene can be suggested. The first step involves excitation of the PhIO to PhIO* followed by its attack on alkene and formation of cyclic intermediate.



Probably light also assists the rupture of the O-I bond leading to formation of epoxide and removal of PhI Since under the reaction conditions, both the oxidant and the alkene, are present in excess, the above pathway does not interfere with the metal-oxo mediated epoxidation [7] and hence the amount of epoxide formed in the photoassisted reaction in absence of catalyst is equal to the excess of epoxide formed in the light assisted reaction in presence of metal catalyst It can thus be concluded that greater yields of epoxide can be obtained by using both, metal complex and light, simultaneously, as catalysts

References

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Table 1 Epoxidation of *cis*-cyclooctene with PhIO in absence or presence of catalyst and light[a]

Run	Catalyst	Reaction Medium[b]	Dark/Light	Epoxide mmol	%Yield[c] Epoxide
1	**1**	AN	Dark	0.01	<1.0
2	**1**	DO	Dark	0.01	<1.0
3	**2**	AN	Dark	0.05	8.3
4	**2**	DO	Dark	0.07	11.7
5	**1**	AN	Light	0.07	11.7
6	**1**	DO	Light	0.1	16.7
7	**2**	AN	Light	0.13	21.7
8	**2**	DO	Light	0.18	30
9[d]	--	AN	Light	0.08	13.3
10[d]	--	DO	Light	0.1	15

a catalyst : oxidant : alkene mole ratio = 1 : 50 : 250, catalyst = 0.012 mmol, rxn time 6h, rxn medium AN/DO + water (6 + 1 ml)

b AN = acetonitrile, DO = dioxane

c based on PhIO charged

d oxidant : alkene mole ratio = 50 : 250