JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 22
1987

Photochemical Epoxidation of Alkenes by Visible Light in a Redox System involving Tetraphenylporphyrinantimony(v) and Water[1]

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Irradiation with visible light of a mixture of an alkene in degassed aqueous acetonitrile containing tetraphenylporphyrinantimony(v) as a sensitizer, methylviologen as an electron acceptor, and hydroxide ion, induced epoxidation of the alkene accompanied by hydrogen evolution, with water acting as the electron donor.

Recent extensive studies on various photoredox systems have led to the finding of systems which evolve hydrogen efficiently upon visible light irradiation.[2,3] Most of these systems involve sacrificial electron donors such as amines, a sensitizer such as a metal complex, and an electron acceptor such as methylviologen which can be coupled with hydrogen evolution catalysed by a noble metal such as colloidal platinum. Here we explore electron donors from the viewpoint of solar energy storage. Much attention has been focused on how a water molecule can be incorporated into an electron donor system.[4] One of the crucial factors in designing a photoredox system is the redox potential of the sensitizer which absorbs visible light. Sensitizers with higher oxidation potentials are expected to be capable of incorporating more types of electron donor into the system which could lead to practical energy storage.

Table 1. Reactivity of alkenes[a].

Alkene	Quantum yield of $MV^{+\bullet}$ formation in aqueous acetonitrile: Neutral	Alkaline[b]
Cyclohexene	0.0	0.16
Cyclo-octene	0.0	0.24
Styrene	0.00010	0.15
Stilbene	0.00005	0.12
Cyclohexa-1,3-diene	0.0047	0.16
2,5-Dimethylhexa-2,4-diene	0.17	0.19

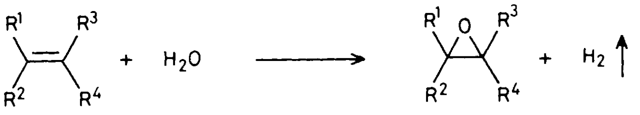
[a] [TPPSb(OH)Br]OH = 1.7×10^{-6} M, [alkene] = 8.3×10^{-4} M, $[MV^{2+}]$ = 8.3×10^{-3} M in degassed $MeCN-H_2O$ (95:5): irradiation at 420 nm. [b] KOH (1.0×10^{-3} M) was added.

Here we report a photochemical epoxidation of alkenes sensitized by tetraphenylporphyrinantimony(v) (TPP-Sb) with an oxidation potential of 1.92 V *vs.* normal hydrogen electrode (N.H.E.) in redox systems with water as the electron donor. Visible light (λ 420 nm) irradiation of the reaction mixture of [TPPSb(OH)Br]OH, methylviologen (MV^{2+}), hydroxide ion (OH^-), and alkene in degassed acetonitrile–water (95:5) induced the reduction of MV^{2+} into its cation radical ($MV^{+\bullet}$). Alkenes were observed to be converted to the corresponding epoxy derivatives. Monoenes such as cyclohexene, cyclo-octene, styrene, and stilbene were reactive only under alkaline conditions, while dienes such as 2,5-dimethylhexa-2,4-diene exhibited high quantum yields even in neutral aqueous acetonitrile (Table 1). Oxidation products of cyclohexene, a typical case, are listed in Table 2 along with the amount of $MV^{+\bullet}$ generated at various OH^- concentrations. At lower OH^- concentrations the amounts of oxidized products in the redox cycle, cyclohexene epoxide and cyclohex-2-en-1-ol, is comparable to that of the reduced

Table 2. Oxidation products of cyclohexene, sensitized by TPP-Sb, upon visible light irradiation[a].

[KOH] added/ 10^{-6} M	$[MV^{+\bullet}]$/ 10^{-6} M	Cyclohexene epoxide /10^{-6} M	Cyclohex-2-en-1-ol /10^{-6} M	Cyclohexane-1,2-diol /10^{-6} M
0	0.0	0.0	0.0	0.0
57	7.4	1.3	3.6	0.0
114	22	1.1	1.9	1.1
289	43	0.79	1.3	1.1
858	140	0.93	1.3	1.2

[a] [TPPSb(OH)Br]OH = 1.7×10^{-6} M, [cyclohexene] = 8.3×10^{-2} M, $[MV^{2+}]$ = 8.3×10^{-3} M in degassed $MeCN-H_2O$ (95:5): irradiation at 420 nm for 60 min.



Scheme 1. Conditions: *h*v, TPP-Sb(v), MV^{2+}, Pt.

product $MV^{+\bullet}$, while the production of $MV^{+\bullet}$ is much enhanced at higher OH^- concentration. This strongly suggests that $MV^{+\bullet}$ production takes place along two major pathways, (i), the redox cycle involving alkene and OH^- and (ii), the reaction enhanced by OH^- without participation of alkene. The former induces the oxidation of the alkene and the latter predominates at higher OH^- concentration. Among the redox cycles involving alkene oxidation, another oxidation product, cyclohexane-1,2-diol, was produced at higher OH^- concentration (Table 2). The diol produced included some *cis* isomer (*cis*/*trans* = 33/67), indicating the partial participation of a sterically regulative reaction such as oxidation on an oxo-type porphyrin complex which could be produced by a deprotonation of the cation radical of OH^- co-ordinated metalloporphyrin.[5] When the reaction flask containing TPP-Sb, alkene, and OH^- was connected with aqueous HCl by a copper wire with platinum mesh electrodes at both terminal ends and a salt bridge between, constant hydrogen evolution was observed upon visible light irradiation. (Scheme 1). Obviously, the water acts as an electron donor and the alkene acts as an oxygen atom acceptor in this photoredox system. Epoxidation of alkenes usually requires strong oxidizing agents using either thermal[6] or photochemical methods.[7] This is the first example of photochemical epoxide formation from an alkene and water without any strong oxidizing agent. Other high valent metaloporphyrins such as $[TPP\text{-}P^{V}(OH)_2]Br$, $[TPPSn^{IV}Cl_2]$, and $[TPPGe^{IV}Cl_2]$ also showed similar reactions.

We thank Professor David G. Whitten at the University of Rochester for stimulating discussions.

Received, 8th April 1987; Com. 461

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