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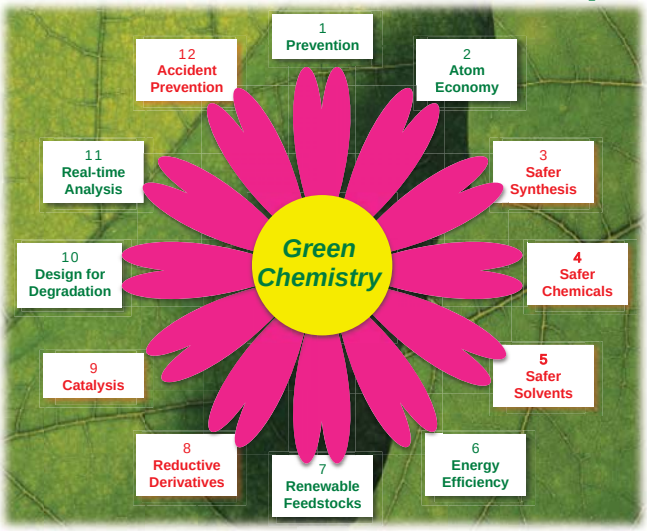
Alternative Protocol for Safer Oxidation in Water: an Effective Epoxydation System

有機溶媒フリー　リスクミニマム酸化反応システム

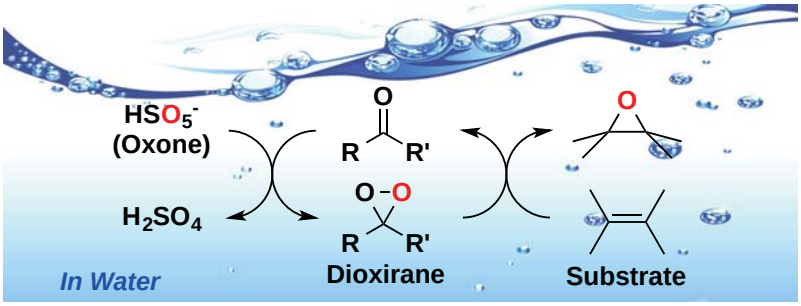
Research Keywords ~ *Green and Sustainable Chemistry, Oxone^R, and Specially Designed Amphiphilic Functional Polymer*

The 12 Principles of *Green Chemistry* [1)]

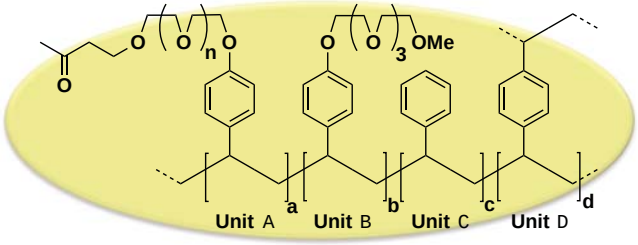


Oxone^R ➔ $2KHSO_5.KHSO_4.K_2SO_4$

- ✓ An inexpensive, easily handled, and water-soluble oxidant.
- ✓ The epoxidation of various alkenes by Oxone is accelerated in the presence of certain ketones as a consequence of *in situ* dioxirane formation.

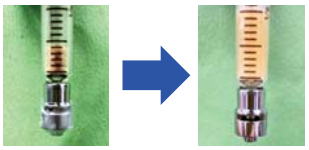


Specially Designed Amphiphilic Functional Polymer



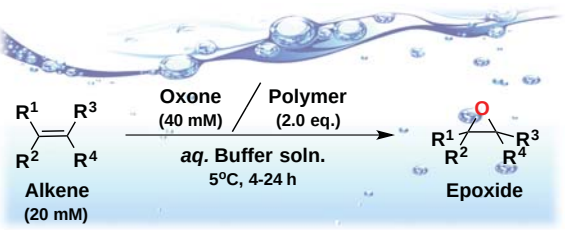
- ✓ Unit A ➔ Acceleration of oxidation by Oxone.
- ✓ Unit B ➔ Hydrophilic moiety.
- ✓ Unit C ➔ Hydrophobic moiety.
- ✓ Unit D ➔ Cross-linker.

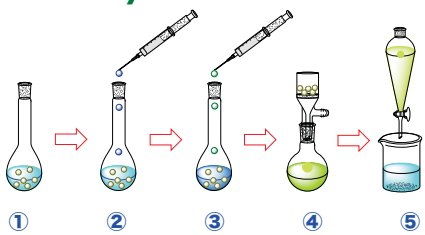
(a:b:c:d = 20:58:20:2, 48:0:50:2, *etc.*)



Swelling of polymer by addition of water

Research Results ~ *Epoxidation of Alkenes by Oxone in the Presence of Polymer in Water*

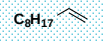
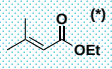




Procedure ➔

① Substrate and polymer in *aq.* buffer.
② Addition of *aq.* Oxone.
③ Quench by addition of *aq.* $Na_2S_2O_3$.
④ Filtration to recover the polymer.
⑤ Extraction to get epoxide.

Substrate		Time/h	pH	Epoxide yield/%
	Blank			20
	Polymer 1	4	10.5	>99
	Polymer 2			>99
	Blank			50
	Polymer 1	4	10.5	>99
	Polymer 2			>99
	Blank			11
	Polymer 1	4	10.5	93
	Polymer 2			94

Substrate		Time/h	pH	Epoxide yield/%
	Blank			0
	Polymer 1	24	7.5	8
	Polymer 2			6
	Blank			0
	Polymer 1	24	7.5	13
	Polymer 2			54

Epoxide yield was determined by GLC analysis.
Polymer 1 ~ a:b:c:d = 20:58:20:2 (n = 3)
Polymer 2 ~ a:b:c:d = 48: 0:50:2 (n = 6)
(*) Oxone = 60 mM

Note ➔

- ✓ Effect of polymer was kept at least after 5 times recycling.
- ✓ Water-insoluble oily alkenes are appropriate substrates for oxidation by Oxone in our reaction system.

1) Andrade, C. K. A.; Dar, A. R. *Tetrahedron* **2016**, *72*, 7375.
2) Masuyama, A.; Yamaguchi, T.; Abe, M.; Nojima, M. *Tetrahedron Lett.* **2005**, *46*, 213.