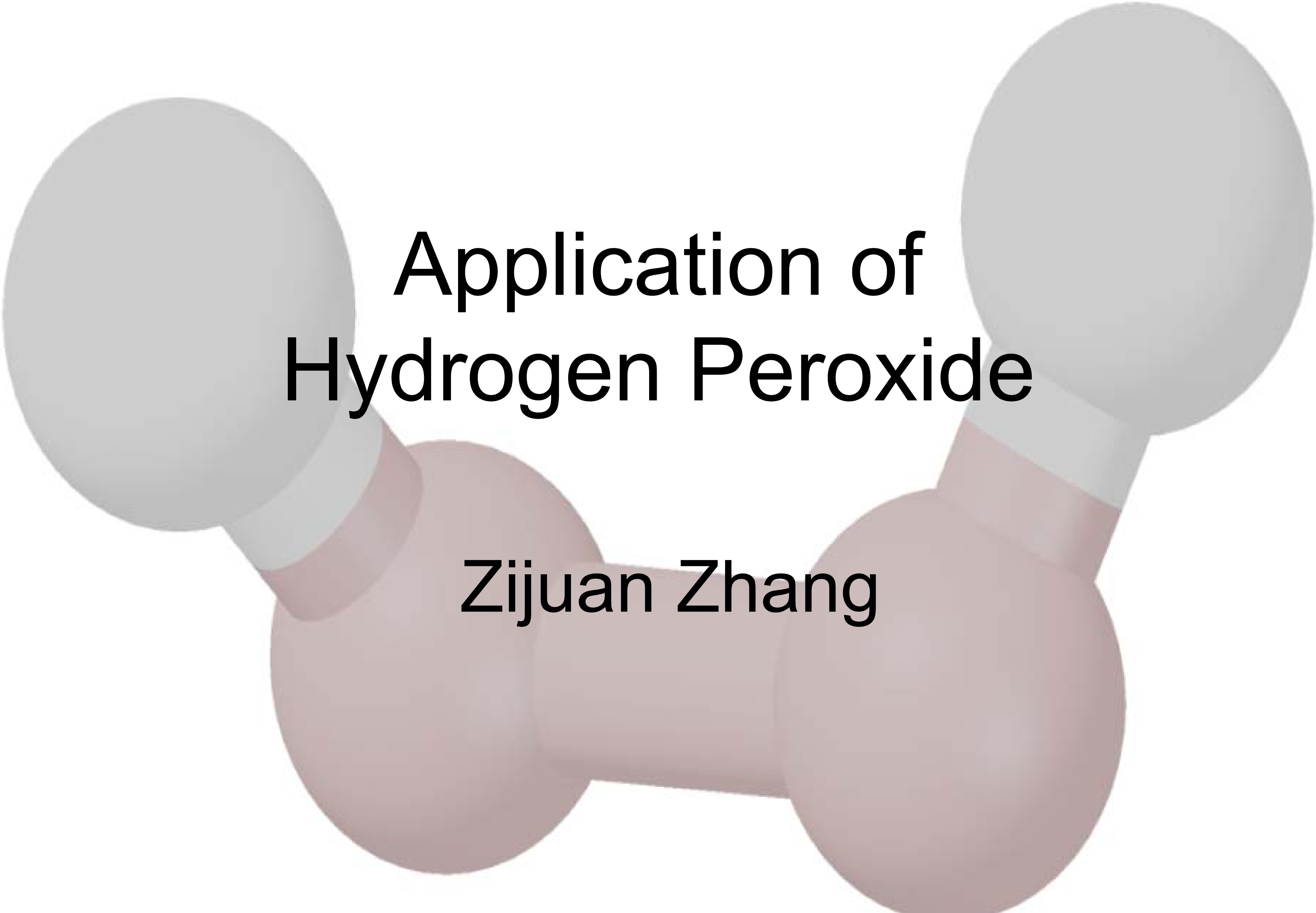
Application of Hydrogen Peroxide

Zijuan Zhang



Outline

- Introduction of Hydrogen Peroxide (H_2O_2)
    - Physical Properties
    - Chemical Properties
    - Decomposition
- Synthesis of H_2O_2
- Application of H_2O_2
    - In Chemical Synthesis
    - In Industry

Physical Properties

Molecular formula	H_2O_2
Molar mass	34.0147 g·mol^{-1}
Appearance	Very pale blue color; colorless in solution
Density	1.4 g·cm^{-3}, liquid
Melting point	-11 °C (262.15 K)
Boiling point	150.2 °C (423.35 K)
Solubility in water	Miscible
Acidity (p*K*a)	11.65
Viscosity	1.245 cP at 20 °C
Dipole moment	2.26 D

http://en.wikipedia.org/wiki/Hydrogen_peroxide

Chemical Properties

Reaction Types:

Decomposition: $2H_2O_2 \longrightarrow 2H_2O + O_2$

Oxidation: $H_2O_2 + M \longrightarrow MO + H_2O$

Addition: $H_2O_2 + A \longrightarrow AH_2O_2$

Reduction: $H_2O_2 + R \longrightarrow RH_2 + O_2$

Substitution: $H_2O_2 + RX \longrightarrow ROOH + HX$

Atom Economy and Byproduct

Oxidant	Active Oxygen(% w/w)	By-Product
O_2	100	H_2O
H_2O_2	47	H_2O
N_2O	36.4	N_2
$NaClO_2$	35.6	NaCl
O_3	33.3	O_2
$NaIO_4$	29.9	NaI
HNO_3	25.0	NO_x
NaClO	21.6	NaCl
t-BuOOH	17.8	t-BuOH
NaBrO	10.5	NaBr
$KHSO_5$	10.5	$KHSO_4$
PhIO4	7.3	PhI

J.L.G.Fierro Angew. Chem. Int. Ed. 2006, 45, 6962

Decomposition of H_2O_2

Commercial grades of hydrogen peroxide are quite stable, typically losing less than 1% relative strength per year.

The primary factors contributing to H_2O_2 decomposition include:

1. temperature (2.2 factor increase for each 10 deg-C);
2. pH (neutral is best, pH ~ 6-8);
3. contamination (especially transition metals such as copper, nickel, zinc or iron);
4. exposure to ultraviolet light.

In most cases, pH and contamination work in tandem as the dominant factors.

Sodium pyrophosphate and sodium stannate are often used as stabilizer.

Container's Material

Recommended materials

- Aluminum
- 99.5% minimum purity alloys with the following Aluminum Association designations: 1060, 1260, 5254, 5652 or 6063
- Stainless steel types 304, 304L, 316, 316L
- Other acceptable materials

  Chemical glass

  Chemical ceramic

  Polytetrafluoroethylene (PTFE; Teflon®[1])

  Polyethylene* (high density, cross-linked, unpigmented and UV stabilized)

  Viton®[1], KelF®[2], Tygon®[3]

  PVC* (temporary systems only)

* For 50% or lower concentration of H_2O_2

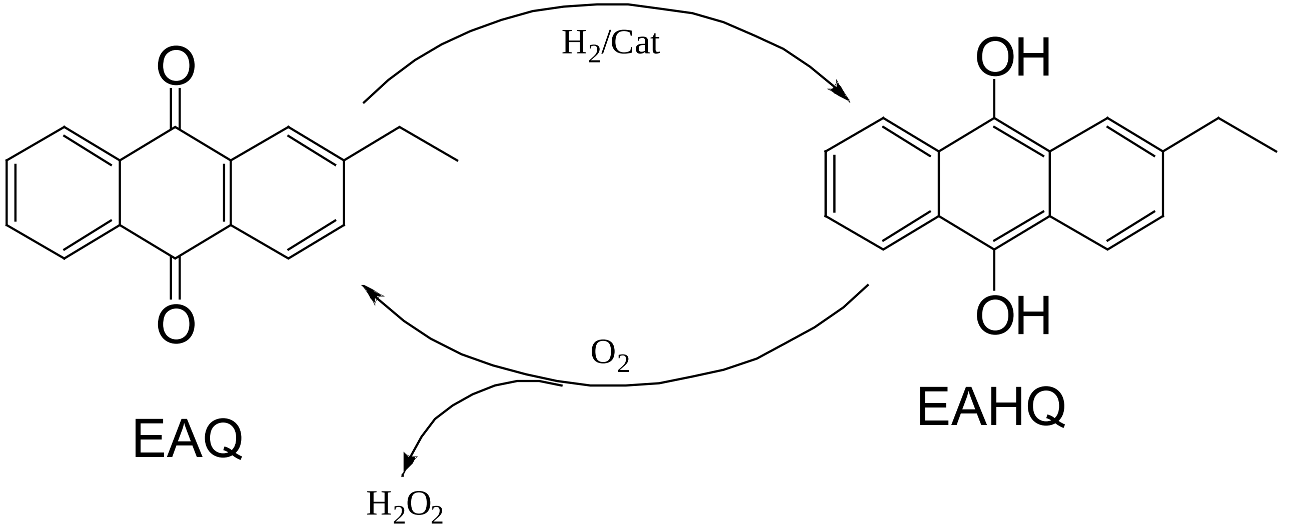
® Registered trademarks of DuPont[1], 3M[2], and U.S. Stoneware[3]

Synthesis of H_2O_2

- First obtained in 1818 by Thenard (barium peroxide + nitric acid)

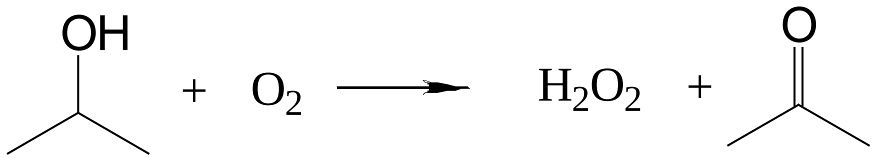
$$BaO_2 + 2HNO_3 \longrightarrow H_2O_2 + Ba(NO_3)_2$$

- Alkylanthraquinone autooxidation (AO) process



Synthesis of H_2O_2

- Oxidation of Alcohols



Shell Chemical, from 1957 to 1980

- Electrochemical Synthesis

Anode: $2OH^- \longrightarrow H_2O + {}^1/_2O_2 + 2e$

Cathode: $H_2O + O_2 + 2e \longrightarrow HO_2^- + OH^-$

Overall reaction: $NaOH + {}^1/_2O_2 \longrightarrow HO_2Na$

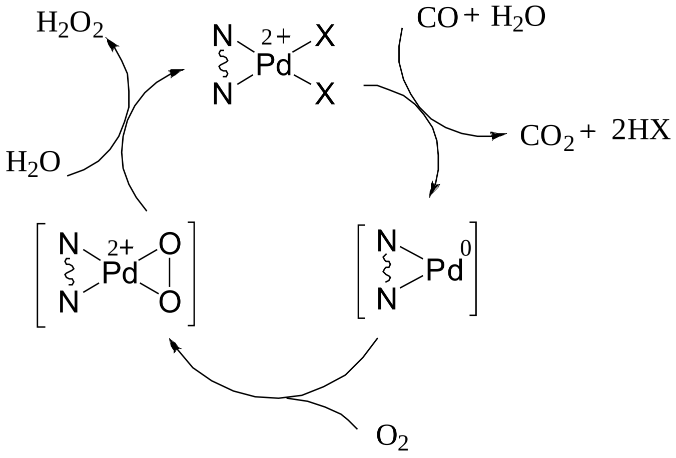
Dow, on-line bleaching

Synthesis of H_2O_2

- Direct Synthesis

$$CO + O_2 + H_2O \longrightarrow H_2O_2 + CO_2$$

$$\left(2CO + O_2 \longrightarrow 2CO_2 \right)$$

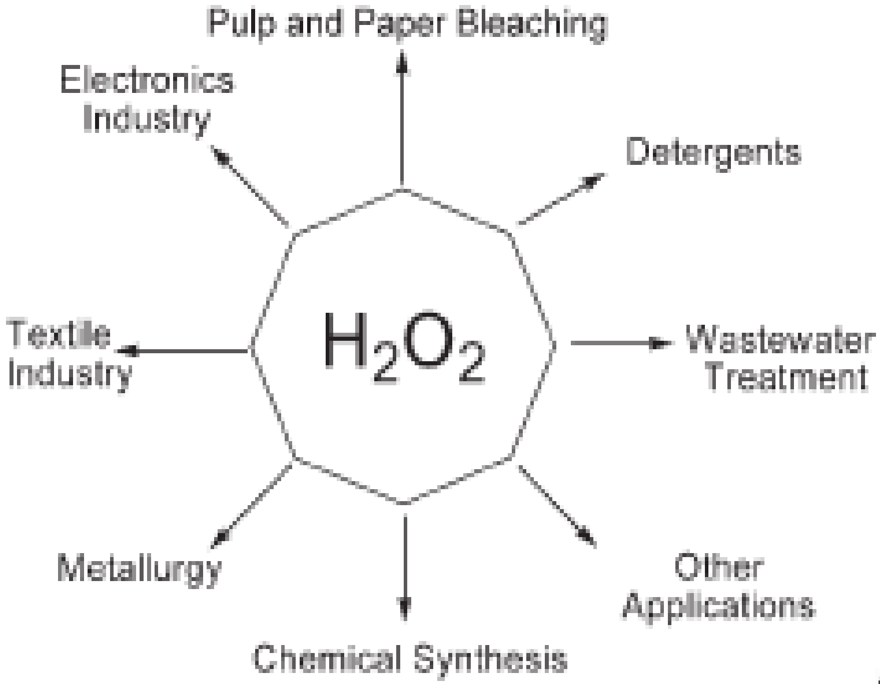


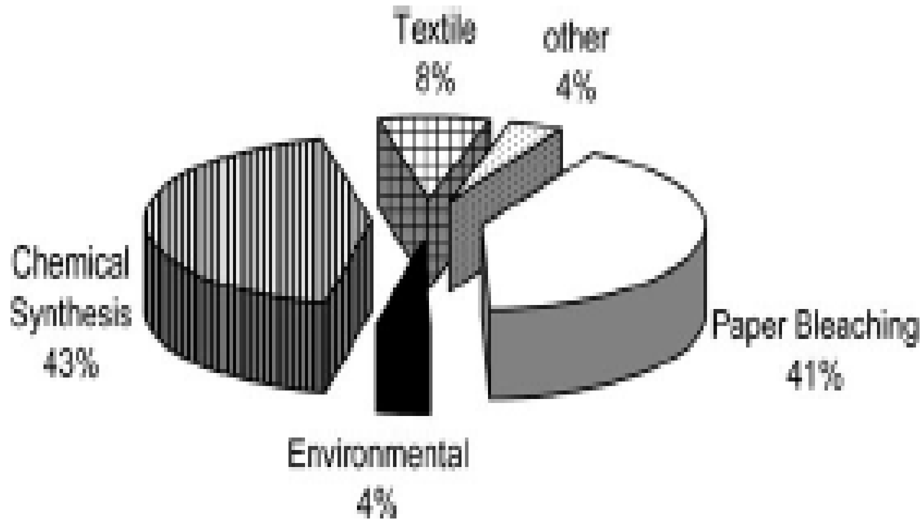
- Other method: Headwaters Technology Innovation

  2007 Greener Reaction Conditions Award

  Process for Direct Catalytic Hydrogen Peroxide Production
  Mike Rueter, Bing Zhou, and Sukesh Parasher, US Patent 7,144,565 B2 (2006)

Application of H_2O_2





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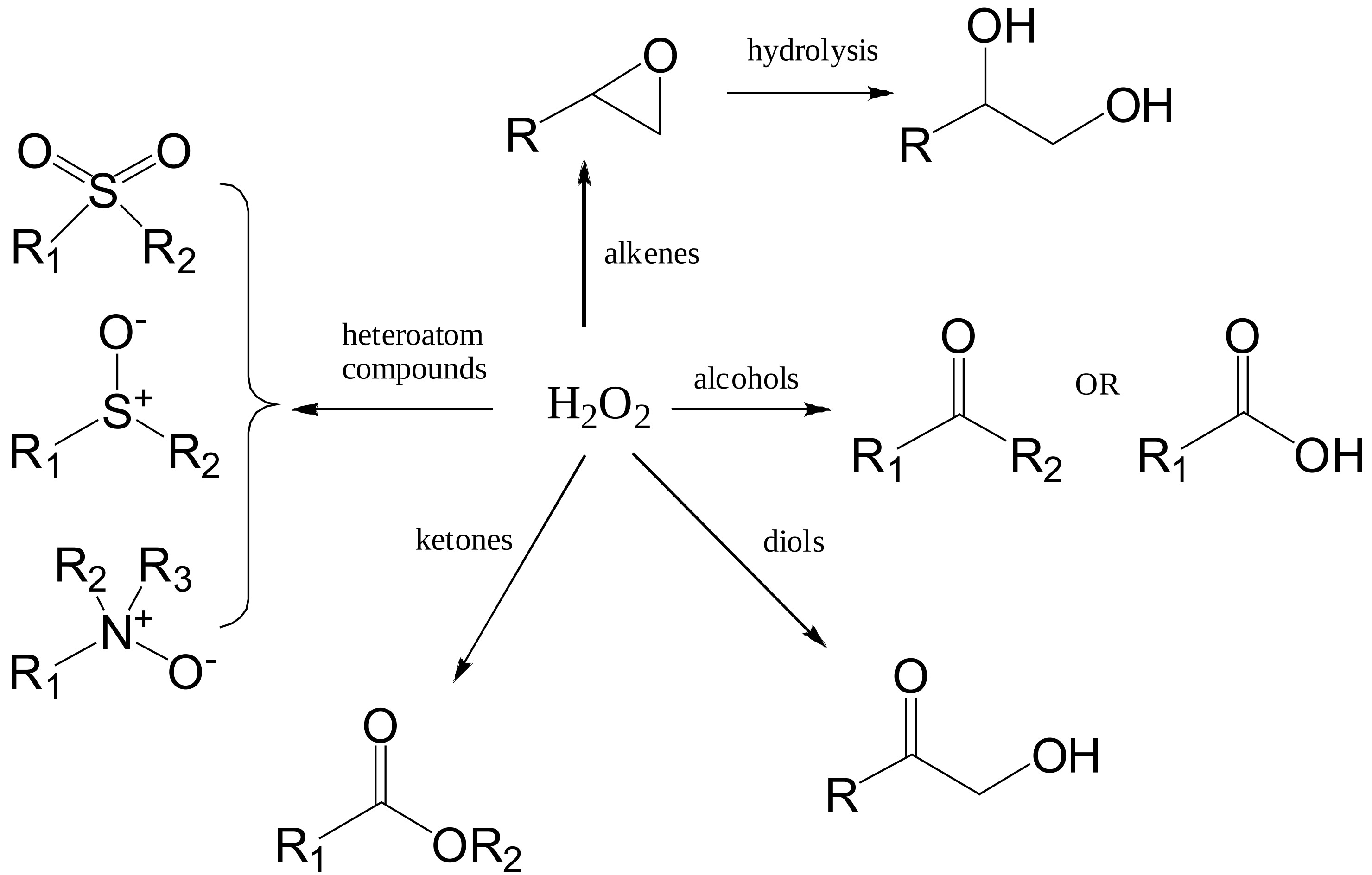
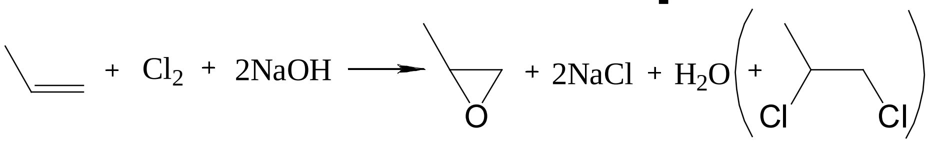
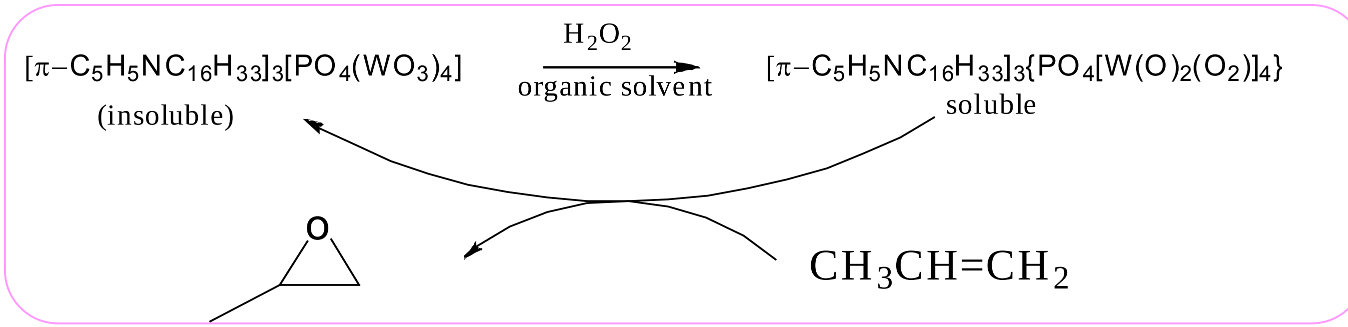
Application in Chemical Synthesis



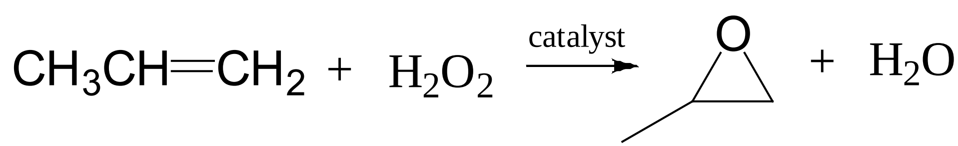
Application in Chemical Synthesis epoxidation



Halcon Method



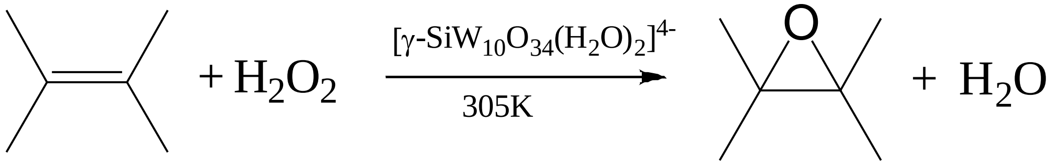
Net reaction



Catalyst	C_3H_6:EAHQ (molar ratio)	Conversion (%)	Selectivity (%)
Fresh	2.5:1	91	94
Cycle 1	2.7:1	87	96
Cycle 2	2.4:1	90	92

Xi Zuwei et al. Science, **2001**, 292, 1139

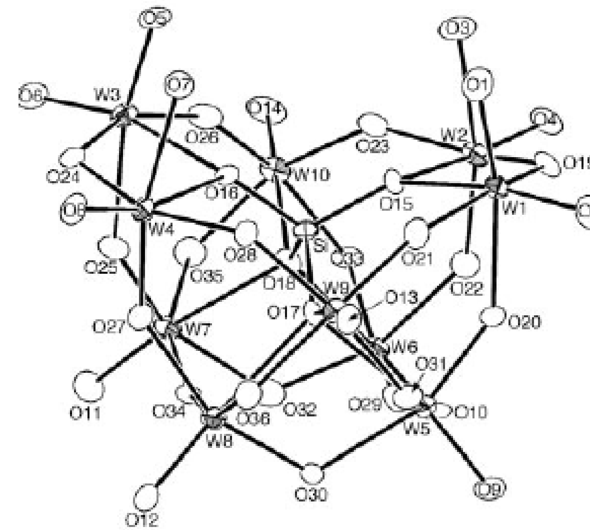
Application in Chemical Synthesis
epoxidation



olefin (5 mmol), $(Bu_4N)_4 \cdot$**1*** (8 μmol), 30% aqueous H_2O_2 (1 mmol), and MeCN(6 ml), @305 K.

Entry	Substrate	Time (h)	Yield (%)	Product [selectivity (%)]	H_2O_2 efficiency (%)
1*		8	90	(>99)	>99
2*		8	88	(99)	>99
3*		9	91	(99)	99
4		10	90	(99)	>99
5		3	>99	(>99)	>99
6		14	91	(99)	99
7		6	84	(>99)	>99
8		4	95	(>99)	99
9		4	>99	(99)	>99
10		2	99	(>99)	>99
11†		4	97	(>99)	>99

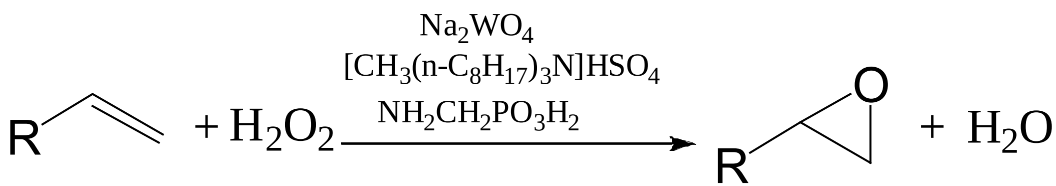
*Propylene (6 atm), 1-butene (3 atm), 1,3-butadiene (2.5 atm). †MeCN (9 mL).



- 0.16 mol% catalyst
- >99% selectivity
- >99% H_2O_2 efficiency
- Broad substrate scope
- Recovered and recycled up to 5 times (no loss of activity)

Kamata, K. et al Science, **2003**,300, 964

Application in Chemical Synthesis
epoxidation



Ryoji Noyori

- High Yield
- Solvent-Free
- Environmental consciousness
- Halide-Free

  Epoxy resin encapsulants for semiconductors are required to be entirely free from chlorides.

Sato, K. et al J. Org. Chem. **1996**, 61, 8310

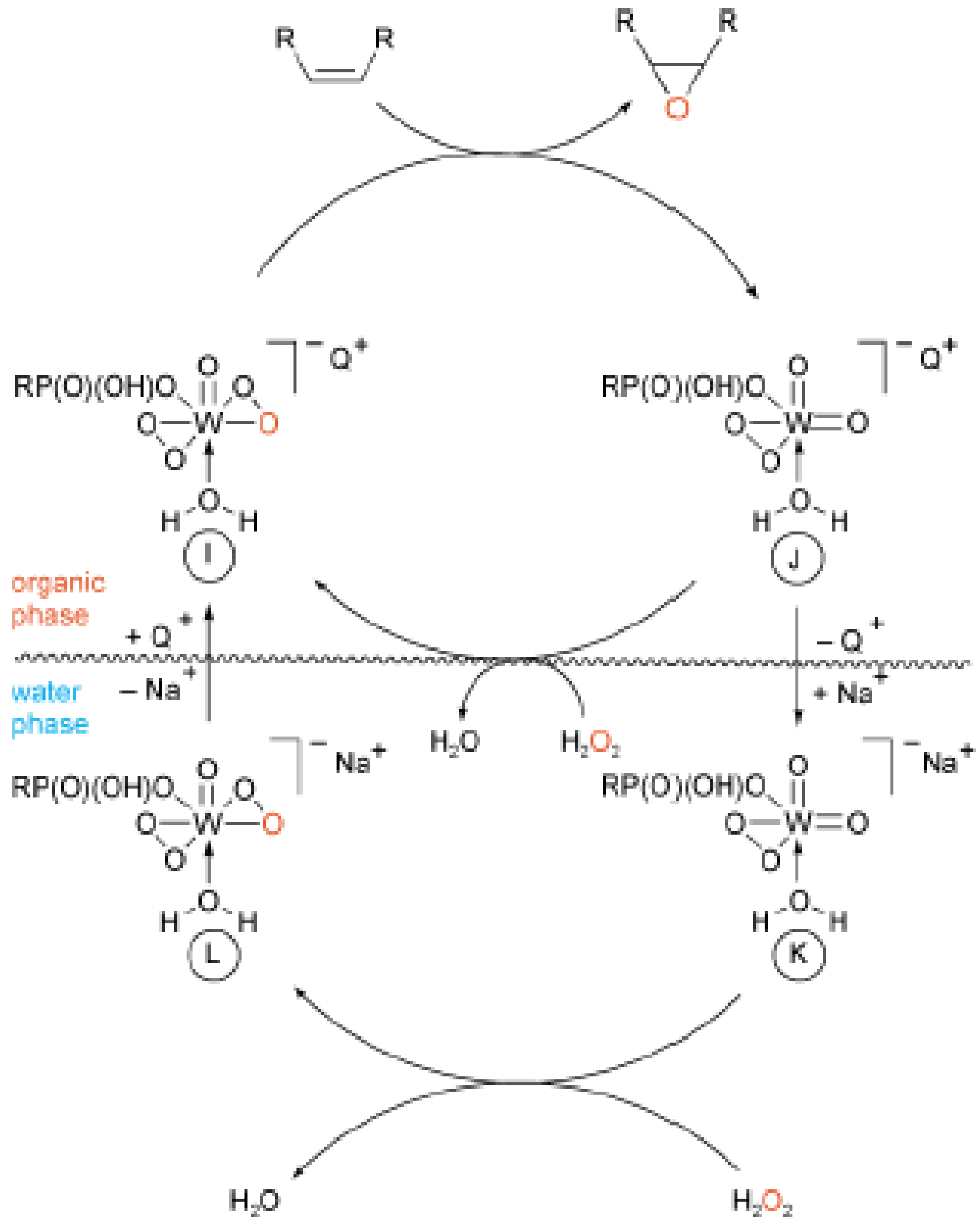
Application in Chemical Synthesis
epoxidation

entry	olefin	mmol	Na_2WO_4, mmol	toluene, mL	time, h	convn,[b] %	yield,[b,c] %
1	1-octene	20	0.4	4	4	96	94
2		20	0.4	0	2	89	86
3		100	2	30	4		86[d]
4	1-decene	20	0.4	4	4	99	99
5		20	0.4	0	2	94	93
6		100	2	30	4		91[d]
7	1-dodecene	20	0.4	4	4	98	97
8		20	0.4	0	2	87	87
9		100	2	30	4		92[d]
10		594	12	0	2		87[d]

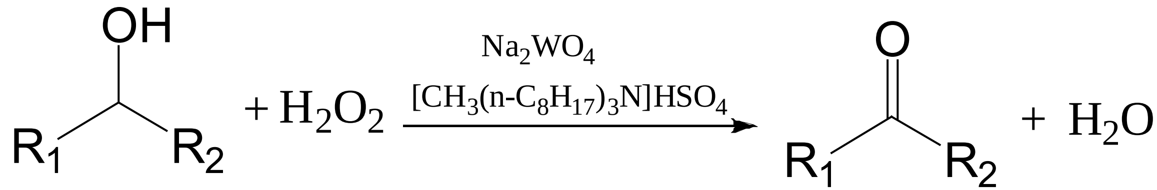
Reaction was run using **30%** H_2O_2, olefin, $Na_2WO_4 \cdot 2H_2O$, $NH_2CH_2PO_3H_2$, and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ in a 150:100:2:1:1 molar ratio at 90 °C with stirring at 1000 rpm. [b] Determined by GC analysis. [c] Based on olefin charged. [d] Isolated by distillation.

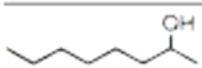
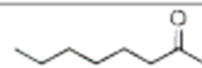
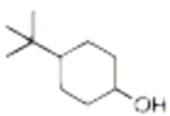
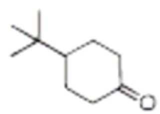
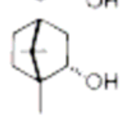
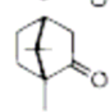
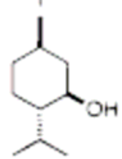
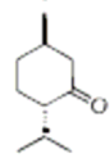
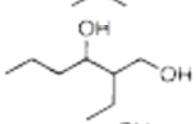
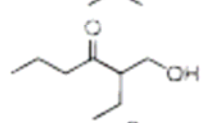
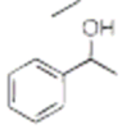
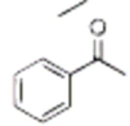
Sato, K. et al J. Org. Chem. **1996**, 61, 8310

Catalytic Cycle of epoxidation



Application in Chemical Synthesis to react with alcohols



alcohol structure	alcohol mmol	Na_2WO_4 and PTC mmol	ketone structure	ketone % yield[b]
	768 768	1.5 1.5		95 95[c]
	640[d]	1.3		96[e]
	648	1.3		84[e]
	640	1.3		93
	684	1.4		83
	819	1.6		96[f]

Unless otherwise stated, reaction was run using alcohol and **30%** H_2O_2 in a 1:1.1 molar ratio with stirring at 1000 rpm at 90 °C for 4 h.

PTC : $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$.

[b] Isolated by distillation.

[c] Reaction with **3%** H_2O_2.

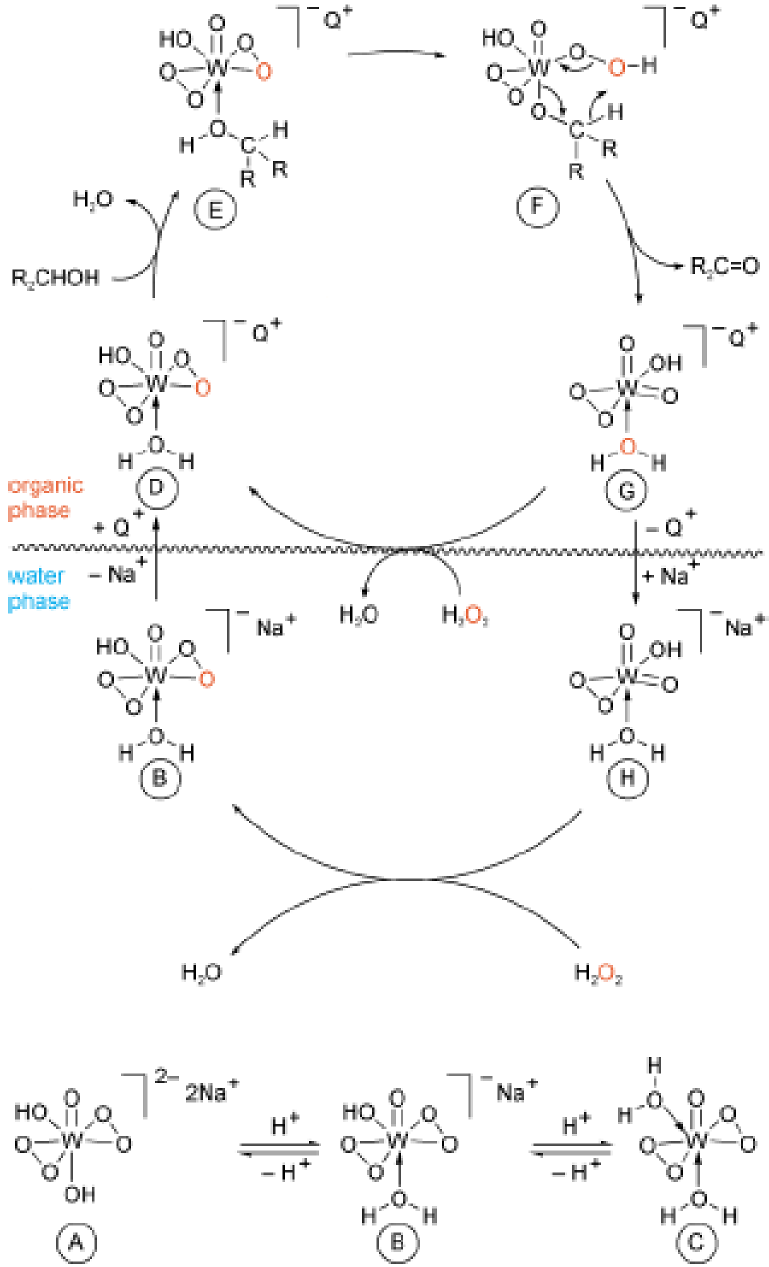
[d] A 1:1 mixture of the cis and trans isomer.

[e] Toluene(100 mL) was used as solvent.

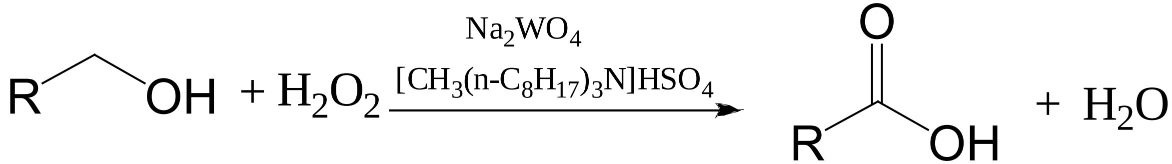
[f] Reaction for 1 h.

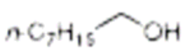
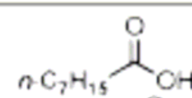
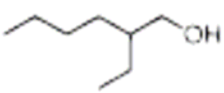
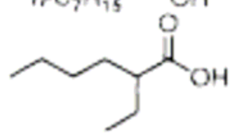
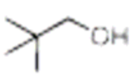
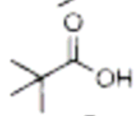
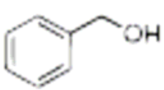
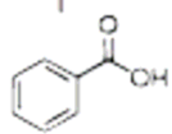
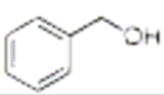
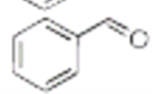
Sato, K. et al J. Am. Chem. Soc. **1997**, 119, 12386

Catalytic Cycle of alcohol oxidation



Application in Chemical Synthesis to react with alcohols



alcohol structure	alcohol mmol	Na_2WO_4 and PTC mmol	product structure	% yield[b]
	768	15		87
	768	15		68
	1130	23		52
	925	19		87[c]
	925	19		86[d]

Unless otherwise stated, reaction was run using alcohol and **30%** H_2O_2 in a **1:1.25** molar ratio with stirring at 1000 rpm at 90 °C for 4 h.

PTC : $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$.

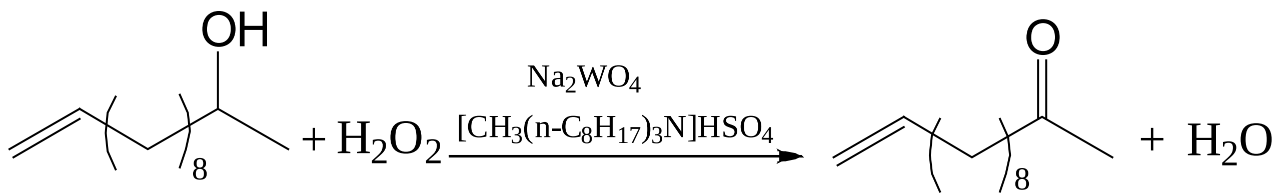
[b] Isolated by distillation.

[c] Isolated by recrystallization

[d] Reaction using alcohol and 30% H_2O_2 in a **1:1** molar ratio. Benzoic acid was produced in <3% yield.

Sato, K. et al J. Am. Chem. Soc. **1997**, 119, 12386

Application in Chemical Synthesis to react with alcohols



alcohol:**30%** H_2O_2:W:PTC =500:750:1:1 (no solvent, 90 °C, 3 h, 1000 rpm) selectively afforded 11-dodecen-2-one (97% yield)

Chemoselectivity of alcohol/olefin

Sato, K. et al J. Am. Chem. Soc. **1997**, 119, 12386

Application in Chemical Synthesis to react with benzylic alcohols

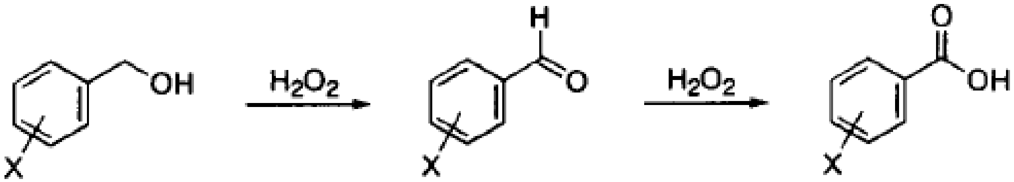


Table 2. Oxidation of benzylic alcohols to benzoic acids[a]

$XC_6H_4CH_2OH$		H_2O_2,	Na_2WO_4 and PTC,		% yield of
X	mmol	mmol (equiv)	mmol (S/C)[b]	time, h	XC_6H_4COOH[c]
p-CH_3O	5	25 (5)	0.05 (100)	12	1[d,e,f]
p-CH_3	819	4092 (5)	8.2 (100)	12	80[d]
H	925	2313 (2.5)	9.2 (100)	5	81[d]
p-Br	535	2138 (4)	5.4 (100)	4	86
p-Cl	701	2806 (4)	7.0 (100)	4	87
p-NO_2	653	2612 (4)	6.5 (100)	4	91

[a] Unless otherwise stated, the reaction was run with **30%** H_2O_2 with stirring at 1000 rpm at 90 °C. PTC = $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$.

Application in Chemical Synthesis to react with benzylic alcohols

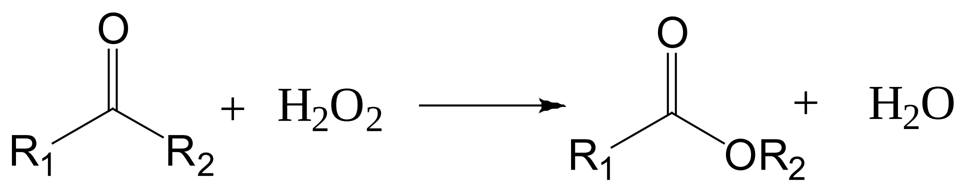
Table 1. Oxidation of benzylic alcohols to benzaldehydes[a]

$XC_6H_4CH_2OH$ X	mmol	H_2O_2, mmol (equiv)	Na_2WO_4 and PTC, mmol (S/C)[b]	time, h	% yield of XC_6H_4CHO[c]
p-CH_3O	724	1086 (1.5)	14.5 (50)	5	90[d,e]
p-CH_3	819	983 (1.2)	4.1 (200)	4.5	91
o-CH_3	819	983 (1.2)	4.1 (200)	4.5	88
H	925	1018 (1.1)	2.8 (330)	3	87
p-Br	535	696 (1.3)	2.7 (200)	4.5	81
p-Cl	701	841 (1.2)	3.5 (200)	4.5	82
p-NO_2	5	10 (2)	0.1 and 0.05 (50 and 100)	17	59[f,g,h]
3,4-Benzo[i]	632	759 (1.2)	3.2 (200)	4.5	82[j,k]

Unless otherwise stated, a 0.1 molar ratio of 5% H_2O_2 to an alcohol was used for activation of the W catalyst, and **30%** H_2O_2 was added dropwise to a mixture of the catalysts and alcoholic substrate with stirring at 1000rpm at 90 °C. PTC = $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$.

Sato, K. et al, tetrahedron letters, **1998,** 39, 7549

Application in Chemical Synthesis to react with ketones



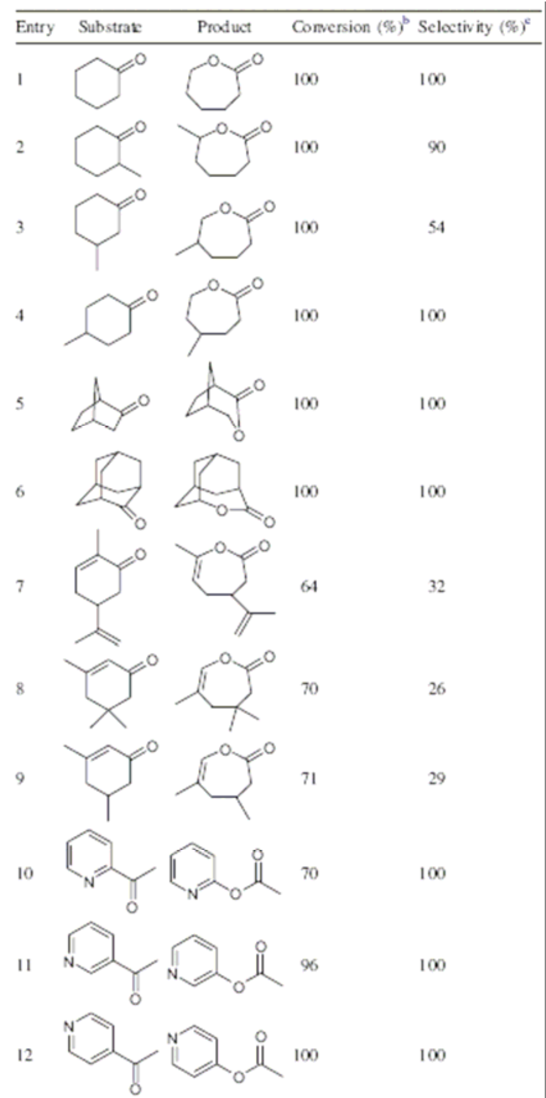
Reaction conditions: ketone: 12 mmol; benzonitrile: 48 mmol; H_2O_2: 2 equiv (30% v/v aqueous solution); catalyst: 0.1 g; T=70 C; surfactant (DBS): 0.6 mmol.

[b] Conversion to lactone after 6 h.

[c] Selectivity to lactone.

$Mg_{0.80}Al_{0.20}(OH)_2(CO_3)_{0.10}\cdot 0.72H_2O$.

- R. Llamas et al. Tetrahedron **2007**, 63, 1435

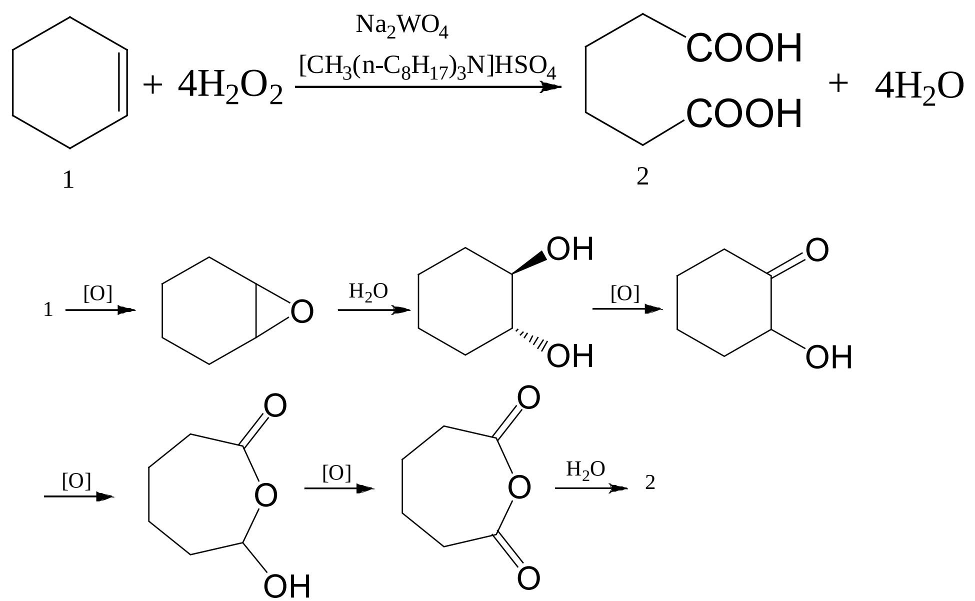


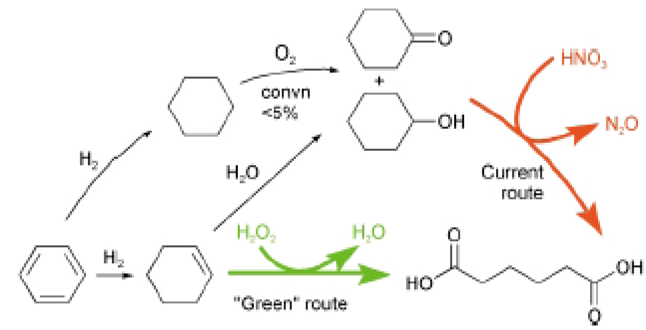
Entry	Substrate	Product	Conversion (%)[b]	Selectivity (%)[c]
1			100	100
2			100	90
3			100	54
4			100	100
5			100	100
6			100	100
7			64	32
8			70	26
9			71	29
10			70	100
11			96	100
12			100	100

Application in Chemical Synthesis multi-step reaction

$$C_6H_{11}OH/C_6H_{10}O + HNO_3 \longrightarrow$$

$$HOOC(CH_2)_4COOH + aN_2 + bNO + cNO_2 + dN_2O$$





cyclohexene, **30%** H_2O_2, $Na_2WO_4 \cdot 2H_2O$, and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ as the PTC (the Olefin : W : PTC molar ratio is 100:1:1) , 1000 rpm and temperature 75° to 90°C, 8 hours, yield 93% (GC). The collection of the crystalline product by filtration followed by drying in air produced colorless, analytically pure **2** in 90% yield.

Thiemens, M. H. et al. Science, **1991**, 251, 932

Sato, K. et al. Science, **1998**, 281, 1646

Application in Chemical Synthesis to react with heteroatoms

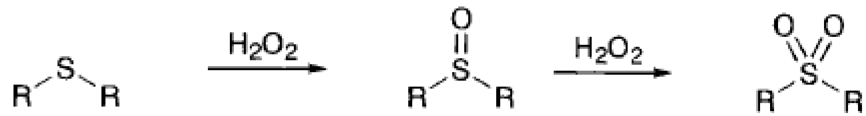
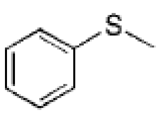
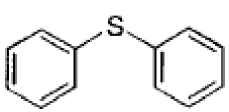


Table 3. Hydrogen peroxide oxidation of sulfides to sulfoxides

Sulfide	Na_2WO_4, $C_6H_5PO_3H_2$, and PTC, mmol (S/C)[a]	H_2O_2 mmol (equiv)	Temp. (°C)	Time (h)	% Yield[b]	
					Sulfoxide	Sulfone
	–	10 (1.0)	35	18	99	<1
	–	68.4 (1.0)[c]	35	18	99[d]	0
	–	11 (1.1)	0	9	31	0
	0.005 (2000)	11 (1.1)	0	9	93	7
	–	10 (1.0)	35	18	99	<1
	–	80.5 (1.0)[c]	35	18	99[d]	0
	–	11 (1.1)	0	9	39	0
	0.005 (2000)	11 (1.1)	0	9	94	6
	–	25 (2.5)	50	12	2	0
	0.005 (2000)	12 (1.2)	25	3	61	21

Unless otherwise stated, reaction was run using sulfide (10 mmol) and 30% H_2O_2. PTC=$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$.

[a] Substrate/catalysts molar ratio.

[b] Determined by ^1H NMR.

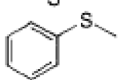
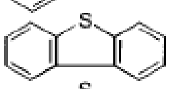
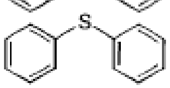
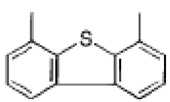
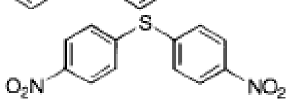
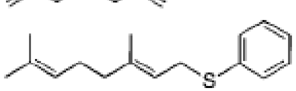
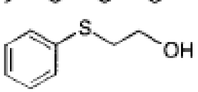
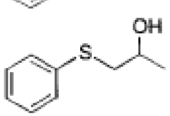
[c] Reaction was run with 10 g of sulfide.

[d] Isolated yield.

Sato, K. et al, tetrahedron, **2001**, 57, 2469

Application in Chemical Synthesis to react with heteroatoms

Table 2. Hydrogen peroxide oxidation of sulfides to sulfones

Sulfide: Structure	Sulfide: mmol	H_2O_2 mmol (equiv.)	Na_2WO_4, $C_6H_5PO_3H_2$, and PTC, mmol (*S/C*)[a]	Temp. (°C)	Time (h)	% yield of sulfone
	10	25 (2.5)	0.01 (1000)	50	1	95[b]
	10	25 (2.5)	0.01 (1000)	50	3	91[b]
	10	25 (2.5)	0.01 (1000)	50	2	97[c]
	10	25 (2.5)	0.01 (1000)	50	3	88[d,e], 97[f,g]
	537[h]	1343 (2.5)	0.54 (1000)	50	2	96[i]
	53.7	134 (2.5)	0.05 (1000)	50	2	92[i], 99[f]
	53.7	134 (2.5)	0.01 (5000)	50	18	87[i]
	10	25 (2.5)	0.01 (1000)	50	24	90[d,i], 98[d,f]
	10	25 (2.5)	0.01 (1000)	50	12	93[f,j]
	10	25 (2.5)	0.01 (1000)	50	24	94[e,j]
	10	25 (2.5)	0.01 (1000)	25	2	93[c]
	10	25 (2.5)	0.005 (2000)	25	24	97[c]
	10	25 (2.5)	0.01 (1000)	25	8	95[c]
	10	25 (2.5)	0.01 (1000)	25	6	91[c]
	10	25 (2.5)	0.005 (2000)	25	24	91[c]
	10	25 (2.5)	0.01 (1000)	25	9	98[c]

Unless otherwise stated, reaction was run using **30%** H_2O_2. PTC=$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$.

a Substrate/catalysts molar ratio.

b Isolated by recrystallization from hexane.

c Isolated by silica-gel column chromatography.

Sato, K. et al, tetrahedron, **2001**, 57, 2469

Application in industry

- Pulp and Paper
- Textile
- Detergent

→ Bleaching

- Environment (Waste Water Treatment)

- Antiseptic

- Metallurgy

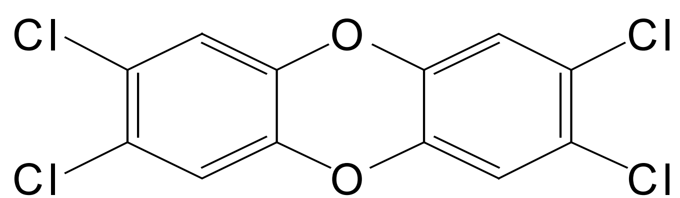
Application in industry -- Bleaching

- Radical reaction

  The color of compounds is a physical property caused by the chemical structure of the molecules.

  The decomposition of hydrogen peroxide involves the formation of free radicals. These reactive intermediates oxidize other molecules and destroy the structure which can absorb the light.

  Compare with Cl_2, $NaClO_2$ and NaClO



dioxine

Application in industry -- Environment

Hydrogen peroxide is used in waste water treatment for the removal of hydrogen sulfide (H_2S), which forms in sewer pipes. The most significant environmental application of hydrogen peroxide is the treatment of a broad variety of industrial wastes . Cyanide (CN^-), thiocyanate (SCN^-), nitrite (NO_2^-), and organic matter (such as TOC) can be efficiently removed by H_2O_2 treatment.

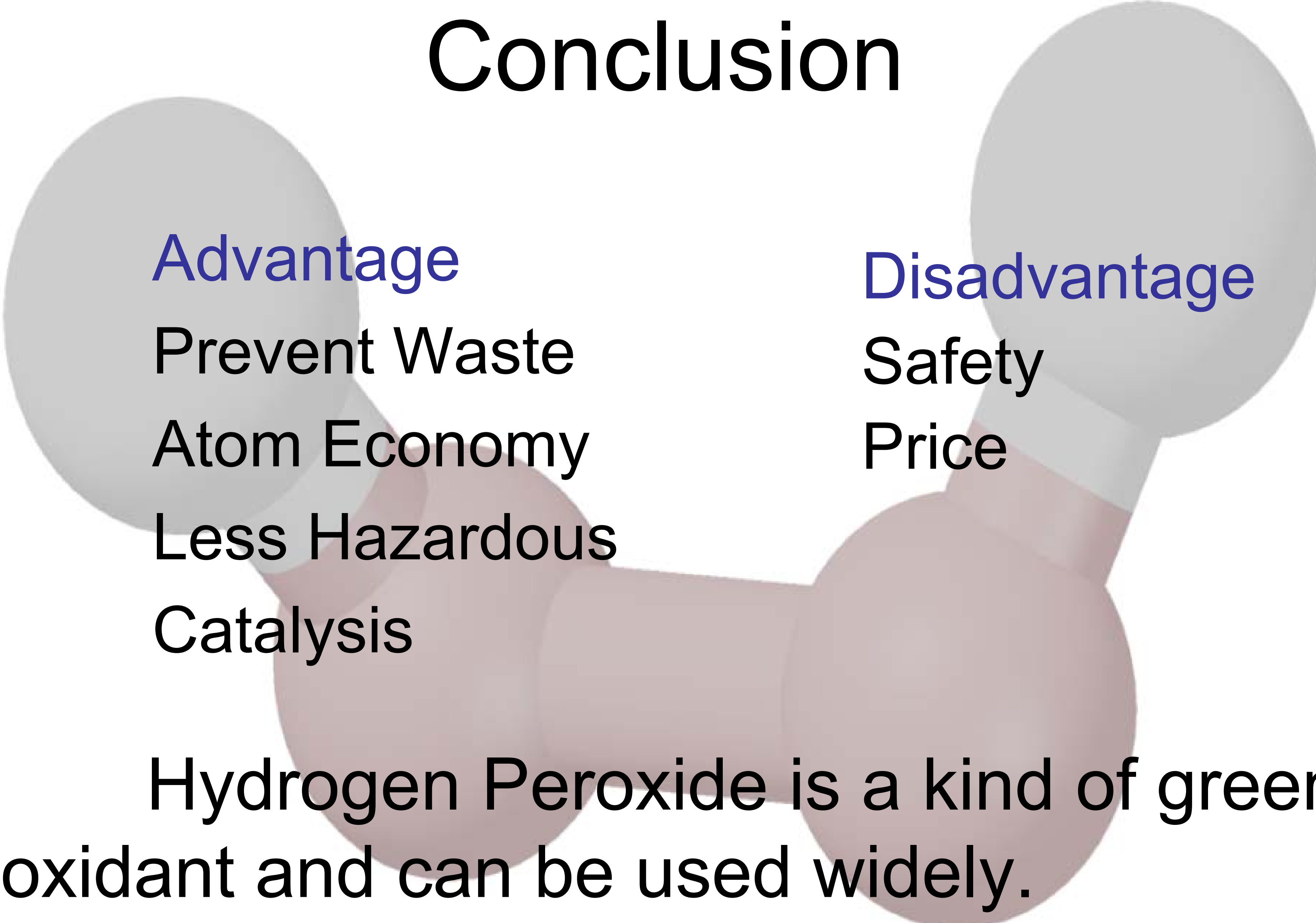
Application in industry
Antiseptic and Metallurgy

$$H_2O_2 + CH_2COOH \longrightarrow CH_2COO\text{-}OH + H_2O$$

Peracetic acid, as a product, it is typically sold as a 5% or 15% active solution for disinfection/sterilization purposes, particularly in the food processing industry.

$$H_2O_2 + H_2SO_4 \longrightarrow H_2SO_5 + H_2O$$

Peroxymonosulfuric Acid is used in the mining and hydrometallurgy industries for digesting ores and separating components, and for destroying cyanide residuals. It is produced onsite at the point of application.



Conclusion

Advantage

- Prevent Waste
- Atom Economy
- Less Hazardous
- Catalysis

Disadvantage

- Safety
- Price

Hydrogen Peroxide is a kind of green oxidant and can be used widely.

Thank You