

Peracetic Acid Bleaching

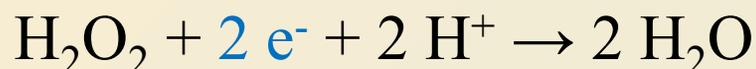


Introduction of Bleaching

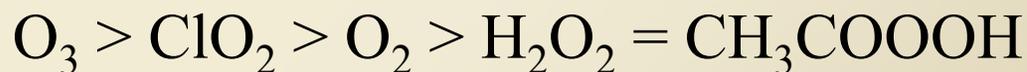
- ❖ Bleaching is a chemical decoloration and delignification process carried out on various types of pulp.
 - ↪ Delignification
 - ↪ Removal of the chromophores
- ❖ At industrial scale, bleaching is performed by chlorine, chlorine dioxide, oxygen, hydrogen peroxide, ozone and peracetic acid.
- ❖ Efficiency: $\text{ClO}_2 = \text{Cl}_2 = \text{O}_3 > \text{CH}_3\text{COOOH} > \text{H}_2\text{O}_2 > \text{O}_2$
- ❖ Often bleaching chemicals are wasted in secondary reactions.

Electron Exchange Theory

- ❖ Ring opening of the aromatic units necessitates the exchange of 4 e⁻
- ❖ # of e⁻ can be exchanged per bleaching molecule



- ❖ # of e⁻ exchanged per molecule decreases in the following order:



Actual Electron Exchange - ClO₂ and O₃

- ❖ 100 g unbleached SW kraft pulp, kappa # from 30 to ~ 4-5
- ❖ 2.3% ClO₂ (0.034 mole) on pulp: $0.034 \times 5 = 0.17 e^-$ is exchanged
- ❖ 1.4% O₃ (0.03 mole) on pulp: $0.03 \times 6 = 0.18 e^-$ is exchanged

Chemicals	% consumed ¹	Kappa number *
ClO ₂	2.3	4.5
O ₃	1.5	3.5
O ₃	1.4	5.0
O ₃	1.3	6.5

¹Chemicals consumed are shown as % on pulp. For example,
For 2.3% ClO₂ consumed: 2.3 g ClO₂ was used to bleach 100g pulp.

* After alkaline extraction: 3% NaOH, 10% consistency, 60 min, 70 °C

Theoretical Electron Exchange - ClO_2 and O_3

- ❖ Assume complete aromatic ring rupture should occur for a full delignification.
- ❖ Assume 200 g/mol of aromatic unit, so 3.75 g lignin in 100 g pulp has 1.87×10^{-2} mole of aromatic unit.
- ❖ Theoretical # of e^- exchanged is $1.87 \times 10^{-2} \times 4 = 0.075$, which is less than half of the actual # of e^- exchanged, 1.7 mole.
- ❖ At least half of the chemicals (ClO_2 , O_3) are used in other reactions, and there is a considerable potential for chemical saving in the bleaching process.

Actual Electron Exchange - CH₃COOOH, H₂O₂ and O₂

They are not possible to perform the same degree of delignification as with ClO₂ or O₃, so comparison should be made for a lower total kappa drop.

	Initial charge (%)	Chemicals consumed ¹ (%)	T (°C)	Time (h)	Kappa #
Pa	3.00	3.00	90	3	13.5
P	1.36	1.30	60	3	17.8
O	Excess	1.50*	110	1	13.5
D	1.07	1.05	70	1	10.2
Z	0.60	0.60	50	-	10.6

Initial kappa #: 24.8;

Kappa # measured after alkaline extraction in the case of Pa, D and Z;

¹Chemicals consumed are shown as % on pulp;

* estimation.

Actual Electron Exchange - CH₃COOOH, H₂O₂ and O₂

of e⁻ exchanged to obtain an one unit kappa

Initial kappa #	Chemical	Total kappa drop	# of e- exchanged /kappa unit	Efficiency %*
24.8	ClO ₂	14.6	0.005	100
24.8	O ₃	14.2	0.005	100
24.8	O ₂	11.3	0.016	30
24.8	H ₂ O ₂	7.0	0.010	50
24.8	CH ₃ COOOH	11.3	0.007	70

* Efficiency of the electron exchange (supposed to be 100% for D).

Efficiency: ClO₂ (=Cl₂) = O₃ > CH₃COOOH > H₂O₂ > O₂

D. Lachenal and C. Chirat, Cellulose Chem. Technol., 39, 5-6, 511-156 (2005)

Conclusion of the Efficiency Calculation

- ❖ Efficiency of the O, P, PAA stages is lower than that was observed with the D and Z stages
- ❖ Lower efficiency means that, for the same number of e^- exchanged, delignification is lower.
- ❖ One reason in the case of P and PAA, could be their decomposition into inactive oxygen.

Bleaching History

- ❖ From chlorine to chlorine dioxide
 - ↪ Generation of organochlorine compounds, including dioxins
 - ↪ ClO_2 was used to bleach ~20% of all kraft pulp (2005).
- ❖ ECF bleaching is now the dominant technology worldwide, accounting for + 75% of bleached kraft pulp globally.
- ❖ TCF process peaked in the mid-1990s
 - ↪ Economic disadvantages
 - ↪ Lack of stricter government regulation and consumer demand
 - ↪ 5-6% of bleached kraft pulp is made using TCF sequences (2005), mainly in Finland and Sweden.
 - ↪ Regulations and consumer demand for TCF pulp and paper are decreasing.

Mechanical vs. Chemical Pulp Bleaching

- ❖ Mechanical pulp: remove the chromophores
 - ↪ Alkaline H_2O_2 and sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) are the most commonly used
 - ↪ The brightness gains are ~temporary
- ❖ Chemical pulp: remove essentially all of the residual lignin
 - ↪ Contain much less lignin than mechanical pulps (<5%)
 - ↪ Sodium hypochlorite → chlorine (1930s) → ECF → TCF (?)

Bleaching Stages for Chemical Pulps

- ❖ A sequence from the 1950s could look like:

CEHEH

- ❖ An example of a modern TCF sequence:

OZEPY

OD(E+O+P)D

D(E+O+P)_ND

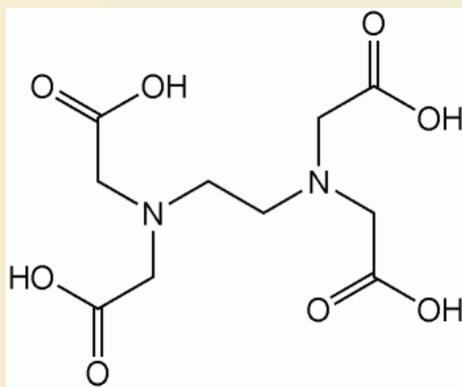
Chemical or process used	Letter designation
Chlorine	C
Sodium hypochlorite	H
Chlorine dioxide	D
Extraction with sodium hydroxide	E
Oxygen	O
Alkaline hydrogen peroxide	P
Ozone	Z
Chelation to remove metals	Q
Enzymes (especially xylanase)	X
Peracids (peroxy acids)	Paa
Sodium dithionite (sodium hydrosulfite)	Y

Purpose of Alkaline Extraction

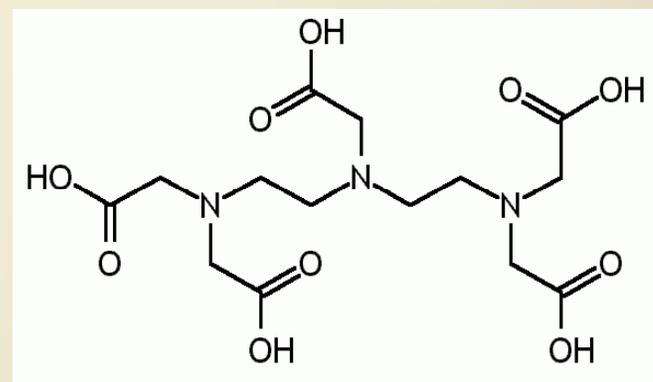
- ❖ After bleaching, lignin is degraded into smaller, oxygen-containing molecules which are generally soluble in water, especially if the pH is greater than 7.
- ❖ These molecules must be removed between bleaching stages to avoid excessive use of bleaching chemicals since they are still susceptible to oxidation.

Purpose of Chelant Wash

- ❖ Chelating agents (EDTA or DTPA), pH at or near 7
 - ↪ Remove transition metal ions on bleaching
- ❖ In TCF bleaching sequences:
 - ↪ Acidic ClO_2 stages tend to remove metal ions
 - ↪ TCF stages rely more heavily on oxygen-based bleaching agents which are more susceptible to the detrimental effects of the metal ions.



Ethylenediaminetetraacetic acid



Diethylenetriaminepentaacetic acid

Whiteness and Brightness

❖ Whiteness

a measurement of light reflectance across all wavelengths of **visible light**. More common in Europe.

❖ Brightness

a measurement of light reflectance of a specific wavelength of **blue light**. More common in North America

Brightness represents a more narrow measurement of light reflectance than whiteness.

Whiteness Index - CIE Whiteness

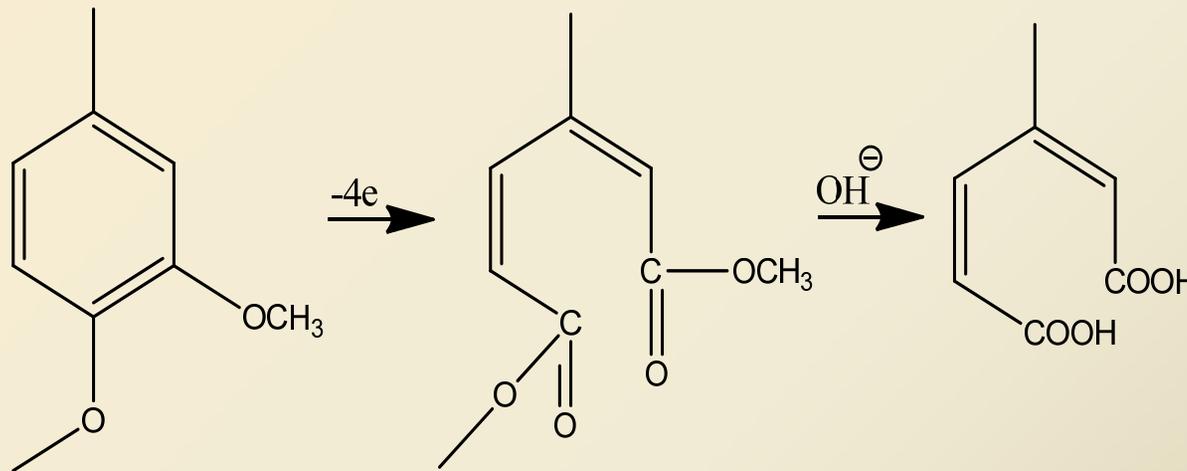
- ❖ CIE Whiteness, developed by the France-based International Commission on Illumination, is commonly used.
- ❖ Better correlates the visual ratings of whiteness for white and near-white surfaces (paper, paint, textile, plastic, etc.).
- ❖ Measurements made under D65 illumination, which is a standard representation of outdoor daylight.
- ❖ For a perfect reflecting, nonfluorescent white material, the CIE Whiteness would be 100.
- ❖ Papers containing fluorescent additives such as Optical Brightening Agents (OBA) will measure above 100.

How Chemical Bleaches Work

- ❖ An oxidizing bleach
 - ↪ Works by breaking the chemical bonds that make up the chromophore.
 - ↪ This changes the molecule into a different substance that either does not contain a chromophore, or contains a chromophore that does not absorb visible light.
- ❖ A reducing bleach
 - ↪ Works by converting sites of unsaturation in the chromophore into single bonds with a reducing agent.
 - ↪ This eliminates the ability of the chromophore to absorb visible light.

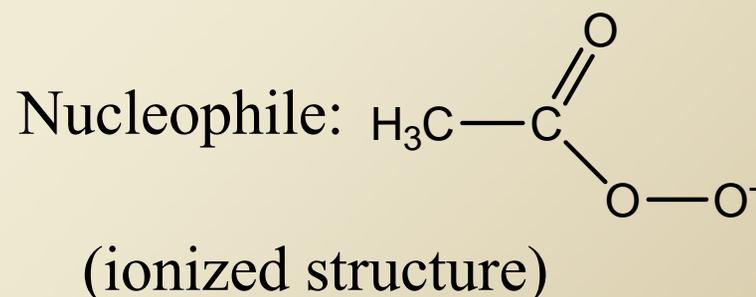
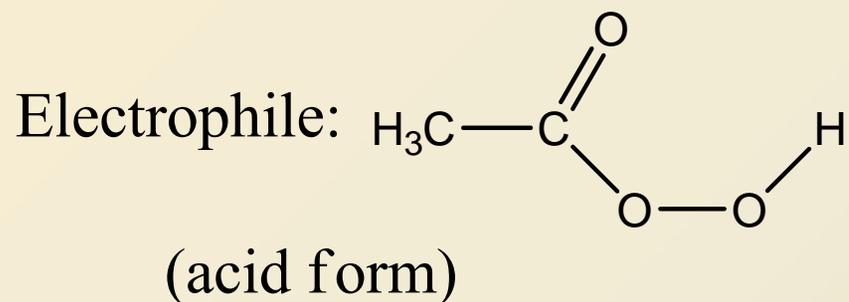
Oxidative Bleaching

For most bleaching chemicals, oxidative delignification can be described primarily by ring opening of the aromatic units



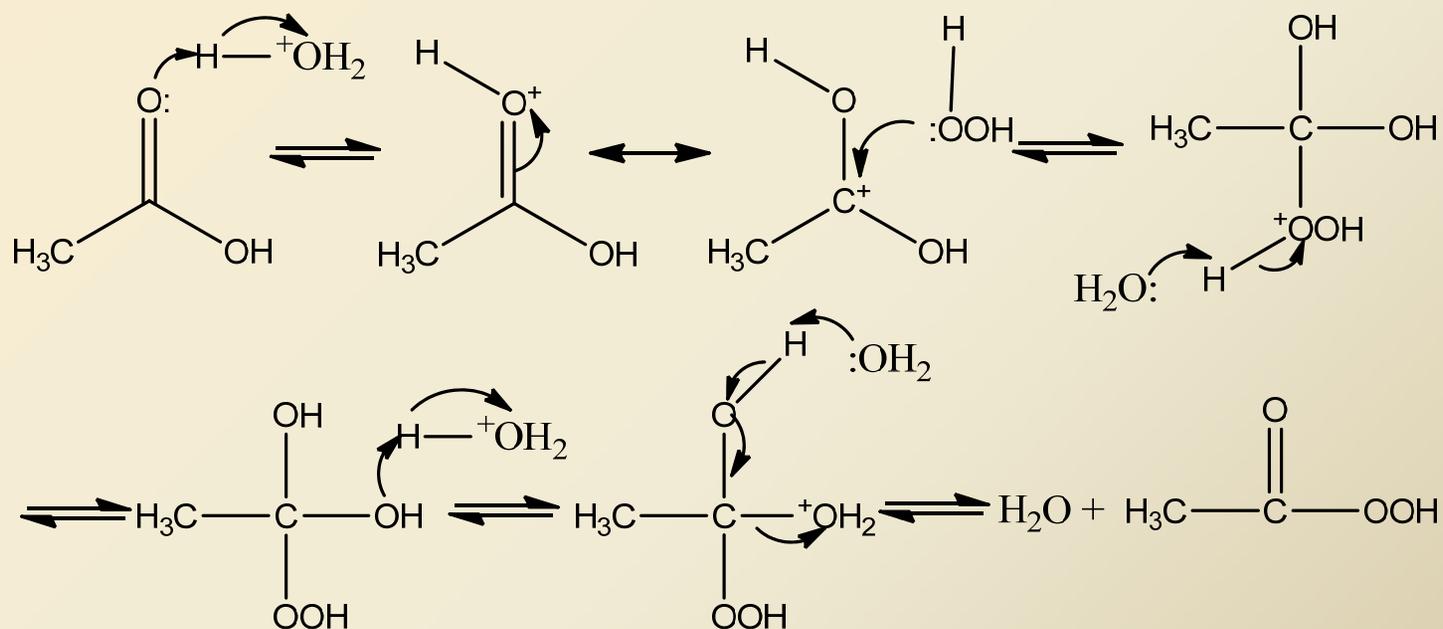
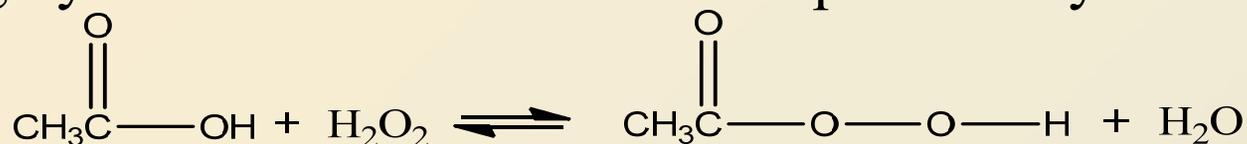
Properties of Peracetic Acid

- ❖ PAA is an organic compound with the formula of $\text{CH}_3\text{CO}_3\text{H}$.
- ❖ It is a colorless liquid with a characteristic acrid odor reminiscent of acetic acid and can be highly corrosive.
- ❖ When pH of water solution = 8.2 (pKa of PAA, weak acid):
Equal amount of ionized PAA and PAA in acid form



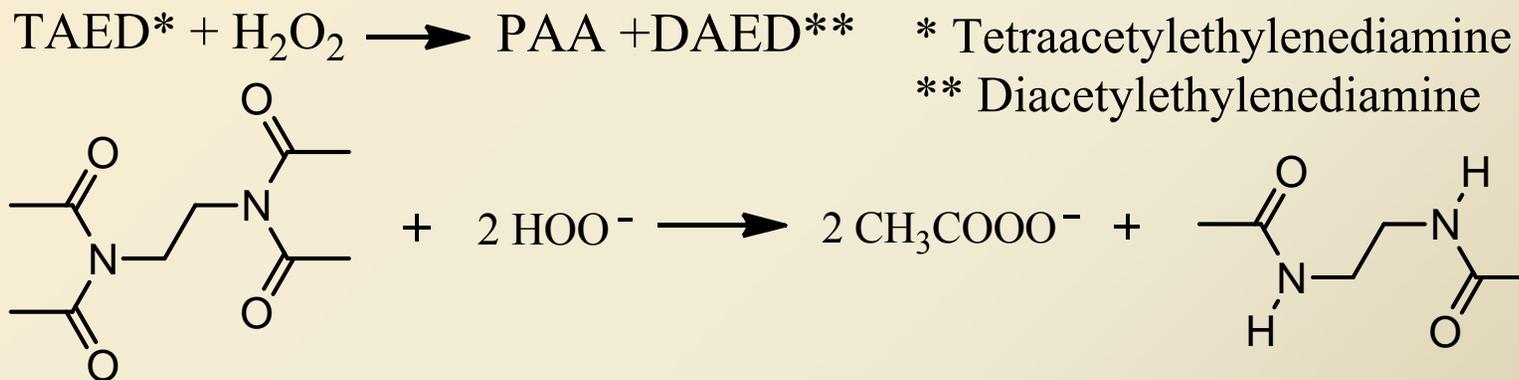
Preparation of Peracetic Acid

- ❖ Continuously feeding CH_3COOH and H_2O_2 into an aqueous reaction medium containing a H_2SO_4 catalyst.
- ❖ The equilibrium constant is 0.37 at room T
- ❖ High yields can be achieved with up to 10 days



Other Preparation Methods

- ❖ Oxidation of acetaldehyde
- ❖ Reaction of acetic anhydride, hydrogen peroxide and sulfuric acid.
- ❖ Reaction of TAED in the presence of an alkaline hydrogen peroxide solution.



- ❖ A series of photochemical reactions involving formaldehyde and photo-oxidant radicals.

PAA Bleaching Condition

- ❖ Used especially for Kraft pulp
- ❖ Usually carried out at relatively low pH ~4,5
 - ↪ PAA is in acid form and acts mainly as an electrophile
- ❖ Usually carried out at relatively low temperature
- ❖ Transition metal content of pulp should be low in order to avoid catalytic decomposition of PAA
- ❖ Sequences: O-Q-Eop-PaaQ-PO
 - O-Q-Paa-P
 - O-Q-P-Paa-P

Evaluation of PAA Bleaching

- ❖ Relatively efficient and selective

Industrial plants for PAA production have been constructed and PAA bleaching is currently in use, either permanently or occasionally, at several mills.

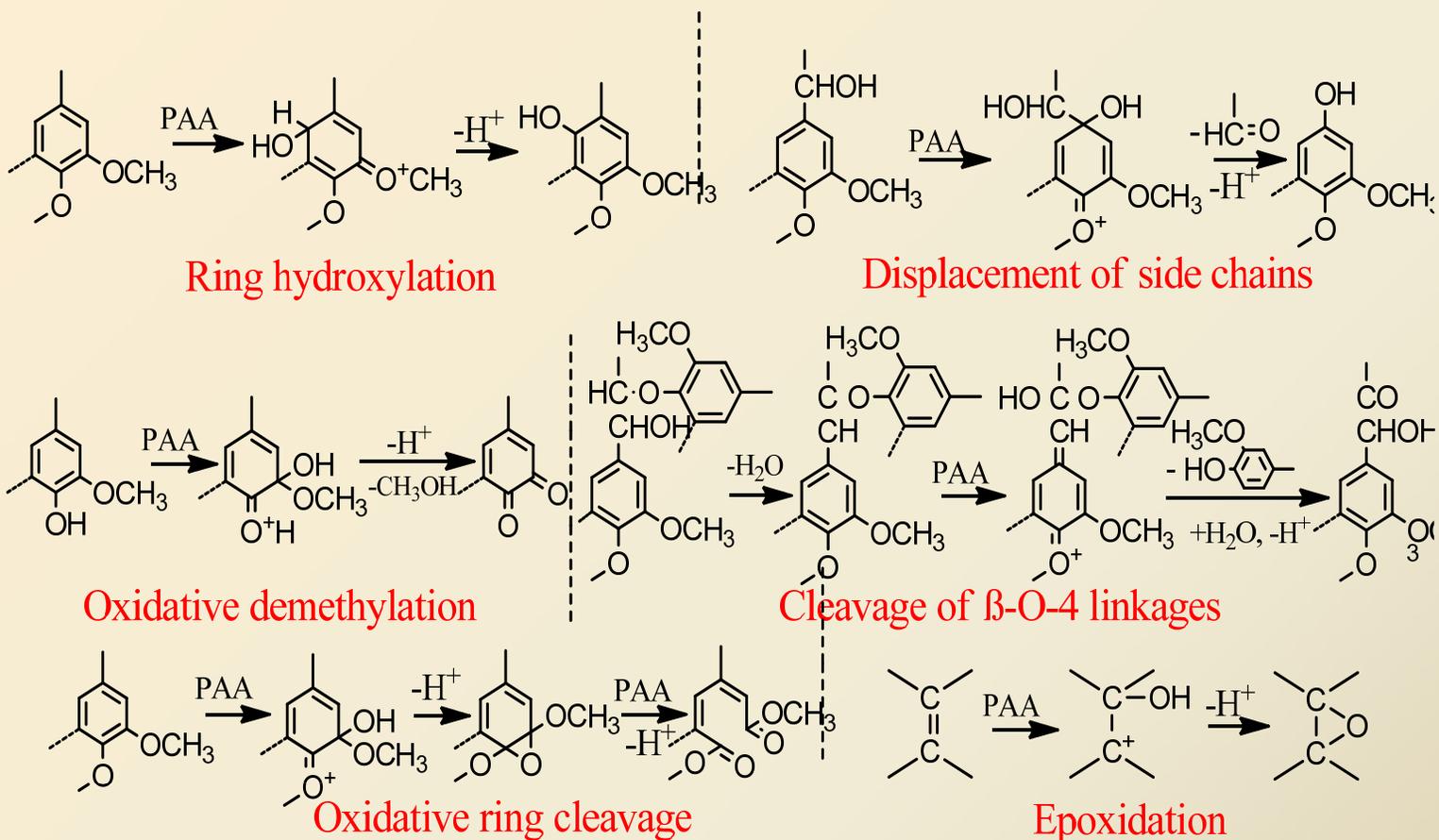
Reason for the High Selectivity of PAA

- ❖ As an electrophile, PAA does not react with aliphatic hydroxyl groups and therefore does not react with most carbohydrates.
- ❖ However, hexenuronic acid groups in kraft pulp xylan have a double bond and thus provide a reactive site for electrophilic attack.
- ❖ Furthermore, the reducing end groups of carbohydrate polymers may be oxidized by PAA.

Reactions Involved in PAA Bleaching

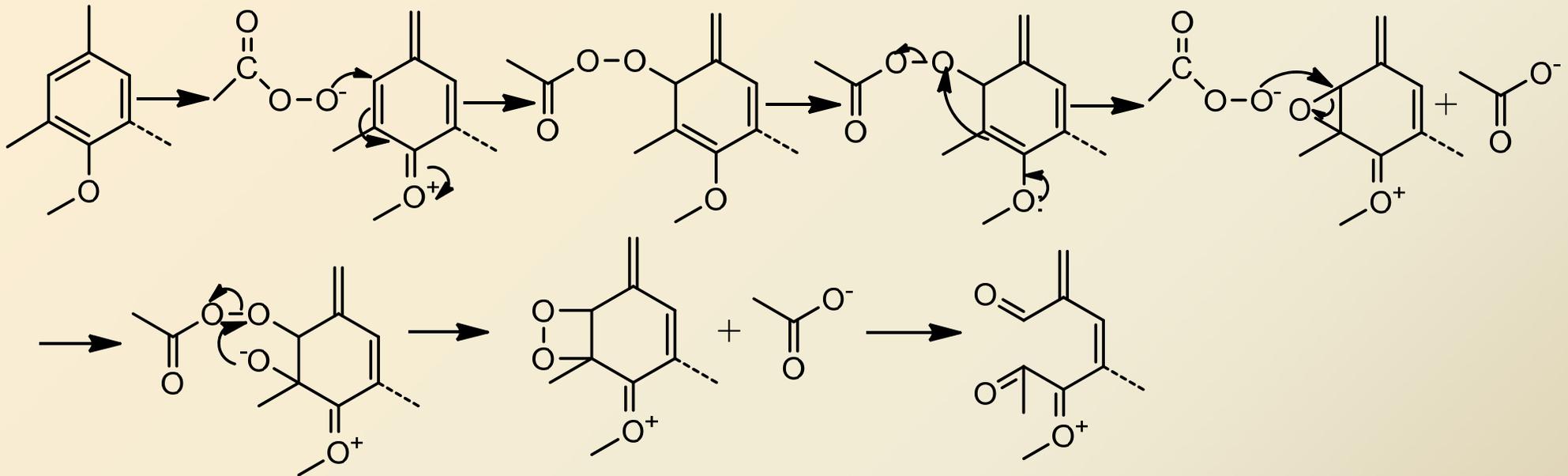
- ❖ At least 6 different types
 - ↪ Hydroxylation, demethylation, aromatic ring opening, side-chain cleavage, β -ether bond cleavage and epoxidation.
- ❖ Main reactions between pulp components and PAA
 - ↪ Delignification (1)
 - ↪ Hexenuronic acid decomposition (2)
- ❖ The rate of (2) is much faster than that of (1), but are both equally T sensitive.

Reactions of PAA with Lignin



Effect of pH on the Whiteness Index

Oxidative ring cleavage (initiated by nucleophilic attack of peracetate ion) is the major reaction under alkaline condition since PAA is more nucleophilic.



- ❖ $\text{pH} < 6.0$, peracetate ion concentration is very low but sufficient for a small increase in WI.
- ❖ $6.0 < \text{pH} < 7.0$, peracetate anion concentration increases and so does the WI.
- ❖ $\text{pH} > 7.0$, PAA decomposition rate is so high that WI begins to decrease.
- ❖ An initial pH between 7.0 and 7.2 is optimum.

An Improved PAA Stage

- ❖ The optimum pH profile for a conventional PAA stage is an initial pH in the neutral range and a final pH of 4 - 5.
- ❖ The new stage has an initial pH of 7, after 20 minutes increasing to pH 9.5, and a final pH in a neutral range.
- ❖ The new stage leads to a higher brightness while the carbohydrate degradation is not affected.
- ❖ Better bleaching effect is obtained at the expense of higher PAA consumption
 - ↪ More consumed in the bleaching reactions
 - ↪ Enhanced decomposition

Comparison of the Two Different Processes

Comparison of conventional (PAA) and improved (PAA_(PH)) processes
(Chelated oxygen delignified pulp, 3% PAA, 20% pulp, 60 min)

	Temperature °C	Brightness % ISO	Viscosity mPa.s	Residual PAA % on pulp
Untreated	-	37.7	23.4	-
PAA	60	64.9	22.3	0.65
PAA _(PH)	60	68.9	21.7	0.03
PAA	80	67.0	22.0	0.29
PAA _(PH)	80	70.8	21.6	0.04

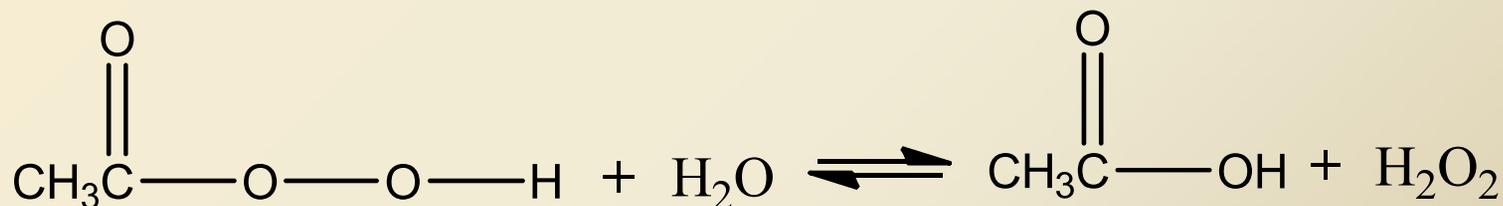
A.V. Heiningen et al. Appita Journal, 51, 5 (1998)

PAA Decomposition

- ❖ pH < 6.0, PAA is very stable (~5.5% decomposition)
- ❖ 6.0 < pH < 8.1, decomposition increases
- ❖ 8.1 < pH < 10.0, decomposition decreases slightly
- ❖ Koubek classified the mechanisms of PAA decomposition in aqueous solution as follows:
 - ↪ Hydrolysis
 - ↪ Base-catalyzed spontaneous decomposition
 - ↪ Trace metal ion catalyzed decomposition
 - ↪ Thermal decomposition

Hydrolysis of PAA

- ❖ No loss of active oxygen content
- ❖ A loss of active bleaching agent, since H_2O_2 is not an effective bleaching agent at low T.
- ❖ Koubek reported that hydrolysis can occur under acidic, neutral, or alkaline conditions, but the mechanisms and kinetics differ.
- ❖ In all cases, however, the rate is 1st order in PAA concentration.



Transition Metal Catalyzed Decomposition

- ❖ Free radicals are likely to be generated by metal catalyzed decomposition of peroxide.



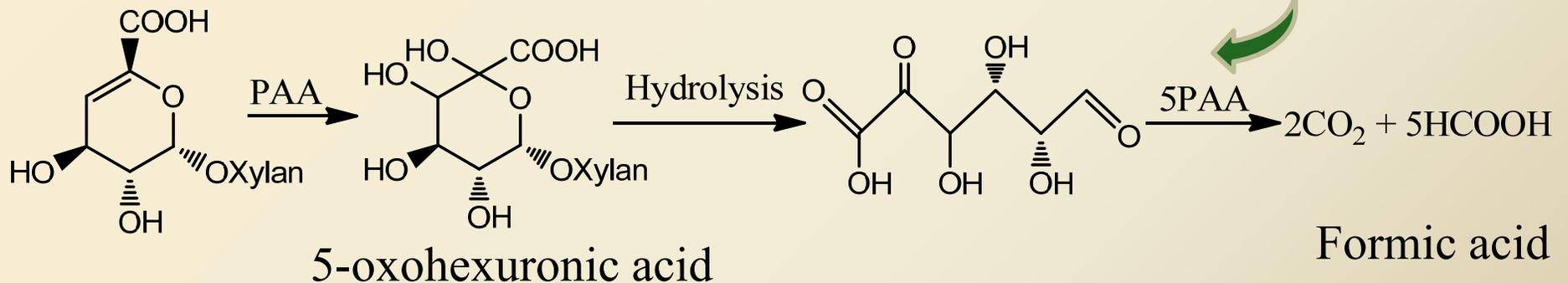
- ❖ Gaseous products are generated through a radical chain mechanism.



- ❖ Decomposition of H_2O_2 could produce hydrolytic decomposition of PAA.

Reaction with Carbohydrates - Hexenuronic Acid Groups

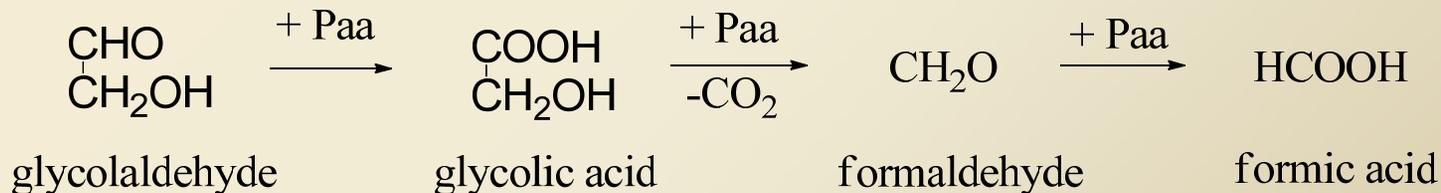
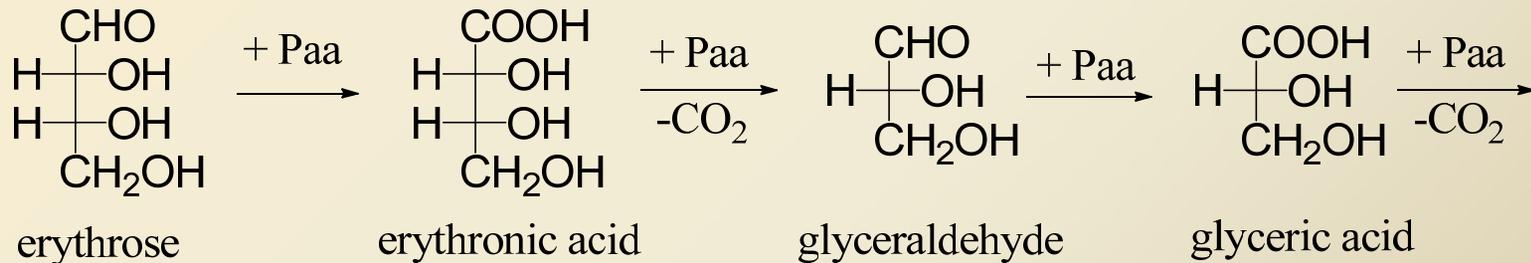
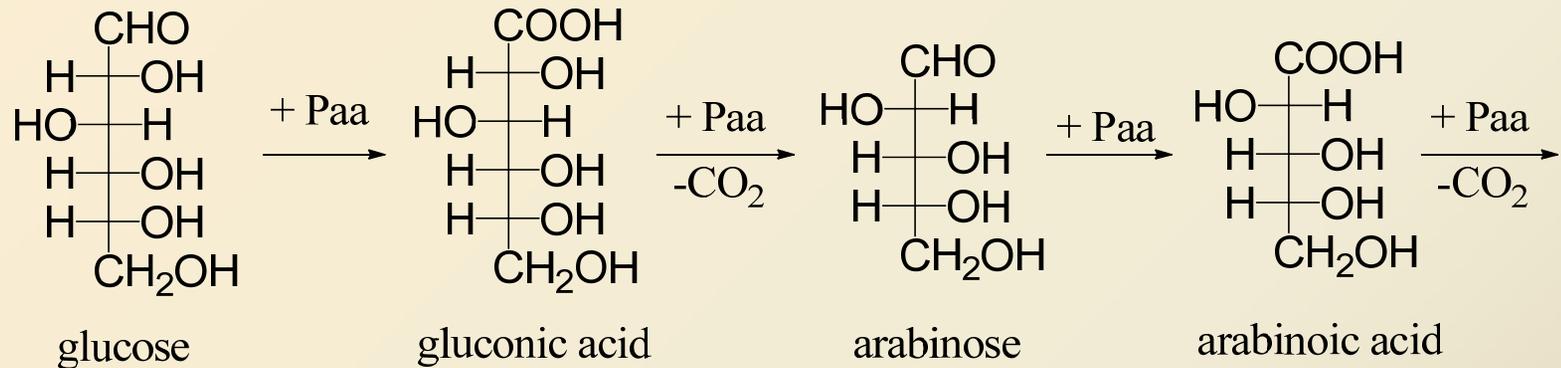
- ❖ It is another main reaction besides delignification and consumes considerable amounts of PAA and therefore it is advisable to remove HexA prior to the PAA stage.
- ❖ At neutral pH: hexenuronate anion and PAA (**much faster**)
- ❖ At low pH: undissociated hexenuronic acid and PAA



The electron density of the conjugated double bond in the carboxylate ion is higher than in the undissociated carboxylic acid group, which implies higher reactivity in electrophilic addition.

Reaction with Carbohydrates - Reducing End Groups

PAA react easily with reducing ends of carbohydrates, however, the amount of that in pulp is relatively low.



K. Poppus-Levlin, Journal of wood chemistry and technology, 20(1), 43-59 (2000)

How to Improve PAA Selectivity

❖ At low pH

- ❧ Increasing the PAA charge: Hydrolysis of carbohydrates is not dependent on the PAA charge, so the selectivity of delignification can be increased.
- ❧ Not increasing temperature: Increases both the rate of delignification and the rate of cellulose depolymerization.

❖ At neutral pH

- ❧ Increasing PAA charge: Increase the rate of delignification.
- ❧ Increasing the temperature: Increased the rate of delignification but had no significant effect on cellulose depolymerization

Comparison of Various Peracids

- Properties of the leaving group affect the electrophilicity and reactivity of peracids with $\text{H}_2\text{SO}_5 > \text{HC}(\text{O})\text{OOH} > \text{CH}_3\text{C}(\text{O})\text{OOH}$
- H_2SO_5 is more electrophilic and it favors aromatic ring hydroxylation
- $\text{CH}_3\text{C}(\text{O})\text{OOH}$ is more nucleophilic and it favors oxidative ring cleavage
- After Paa Pulp Bleaching:
 - *Residual lignin has a higher amount of PhOH*
 - *The amount of acid groups is increased thereby improving the hydrophilicity of lignin.*
 - *Due to the cleavage of lignin side chains the MW of residual lignin is decreased improving the hydrophilicity.*
 - *Pulp is more bleachable*