O_3
Ozone Bleaching Highlights

INTRODUCTION

- Ozone is a very powerful oxidizing agent and the biggest challenge in using it to bleach wood pulp. Ozone can react with sites of unsaturation in lignin, including those within aromatic rings.

- Ozone is a good reagent to allow pulp to be bleached without any chlorine-containing chemicals (totally chlorine-free, TCF)

Background of ozone

- In 1839 SchoÈnbein identied the odor rising from the anode during the electrolysis of water as an attribute of a new chemical compound which he gave the name ozone.

- **Physical properties**

  Ozone is a pale blue gas, slightly soluble in water and much more soluble in inert non-polar solvents such as carbon tetrachloride or fluorocarbons, where it forms a blue solution.

  Most people can detect about 0.01 ppm of ozone in air where it has a very specific sharp odor.
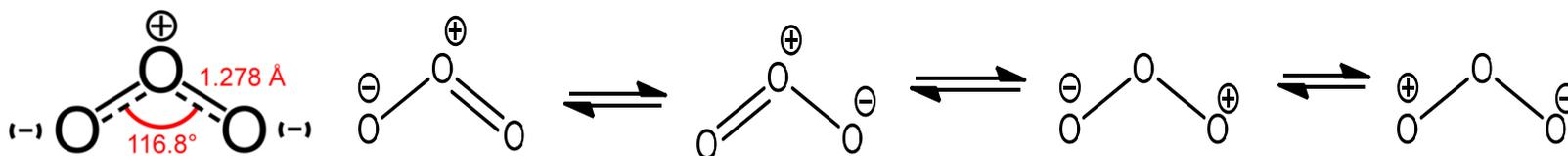
Background of Ozone

- **Physical properties**

Properties	
Molecular formula	O_3
Molar mass	47.998 g·mol^{-1}
Appearance	bluish colored gas
Density	2.144 g/L (0 °C), gas
Melting point	80.7 K, −192.5 °C
Boiling point	161.3 K, −111.9 °C
Solubility in water	0.105 g/100mL (0 °C)

Background of Ozone

- **Structure**

  Ozone is a bent molecule, similar to the water molecule. The O – O distances are 127.8 pm. The O – O – O angle is 116.8°. The central atom is *sp²* hybridized with one lone pair. Ozone is a polar molecule with a dipole moment of 0.5337 D. The bonding can be expressed as a resonance hybrid with a single bond on one side and double bond on the other producing an overall bond order of 1.5 for each side.

Background of Ozone

- **Chemical properties**

  Ozone is one of the strongest oxidizing agents known, exceeded in electronegative oxidation potential by F_2 and the oxygen atom, far stronger than O_2 . Ozone is formed from oxygen in a strongly endothermic reaction and decomposes easily into molecular and atomic oxygen, with a half-life of about half an hour in atmospheric conditions.

Background of Ozone

- Ozone can be generated from oxygen, air or from other N_2/O_2 mixtures. The first step towards ozone formation in gas discharges is the dissociation of O_2 molecules by electron impact

- Many technical ozone generators use cylindrical discharge tubes of about 20-50mm diameter and 1-3m length. Large ozone generators use several hundred discharge tubes.

- Large ozone generating facilities produce several hundred kg ozone per hour at a power consumption of several megawatts. The capacity of a big ozone generator is up to 100 kg/h. The main applications are in water treatment and in pulp bleaching.

U. Kogelschatz et al. Pure Appl. Chem. 1999, 71, 1819-1828
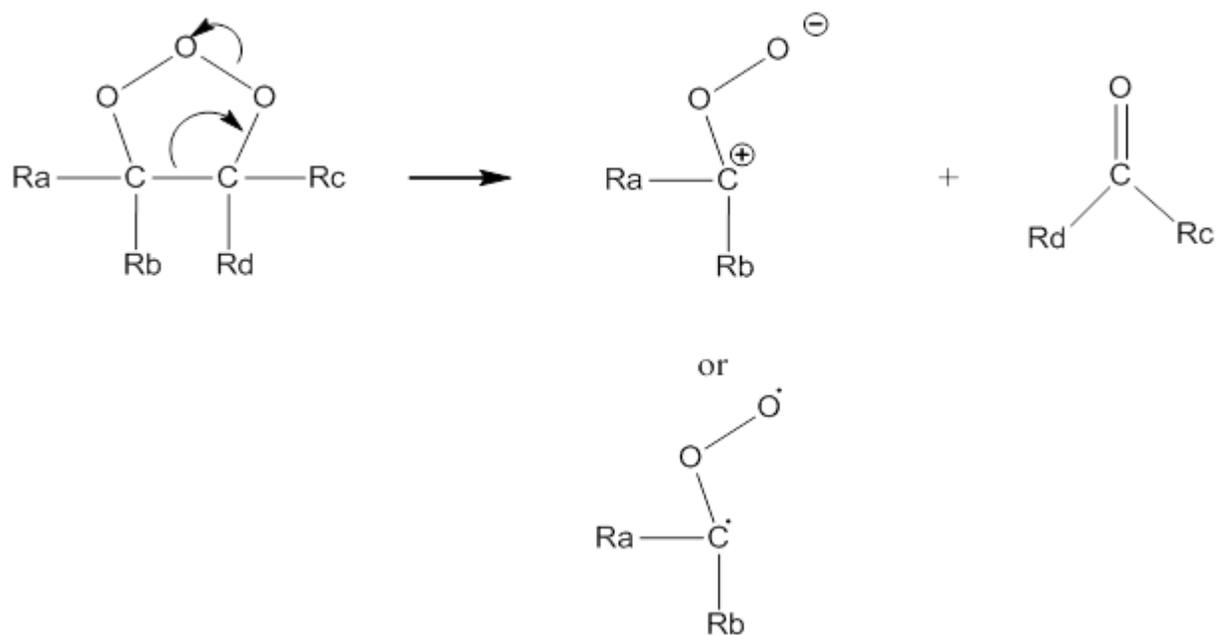
O_3 Reactions With Lignin

- Reactions of ozone with alkenes proceed by way of the Criegee mechanism

  The reaction begins with a 1,3 dipolar concerted addition reaction across the double bond to form a highly unstable 1,2,3-trioxolane, or primary ozonide
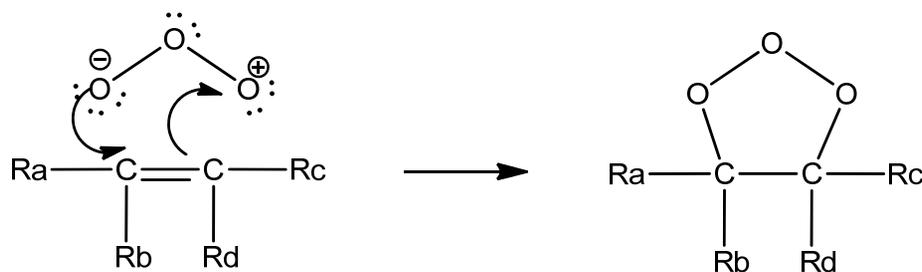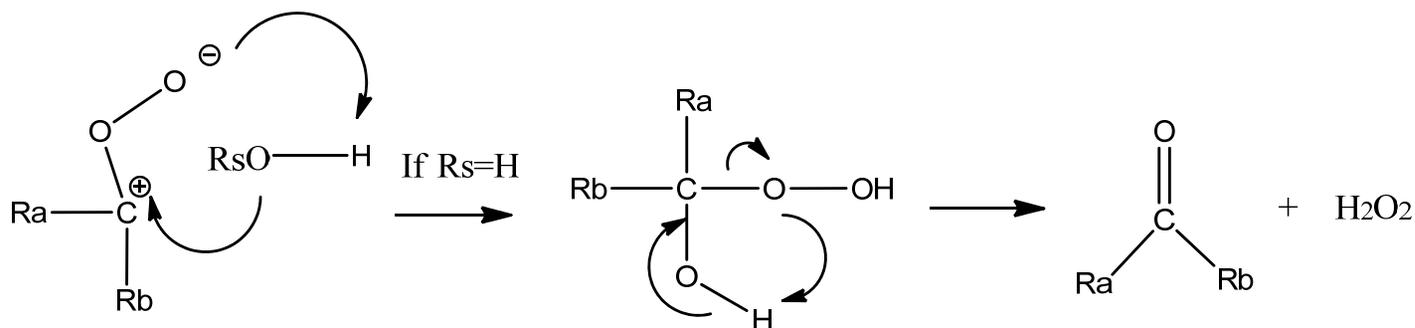
Reactions With Lignin

The primary ozonide may be cleaved at the C-C bond to produce a carbonyl and a carbonyl oxide zwitterion or radical pair.
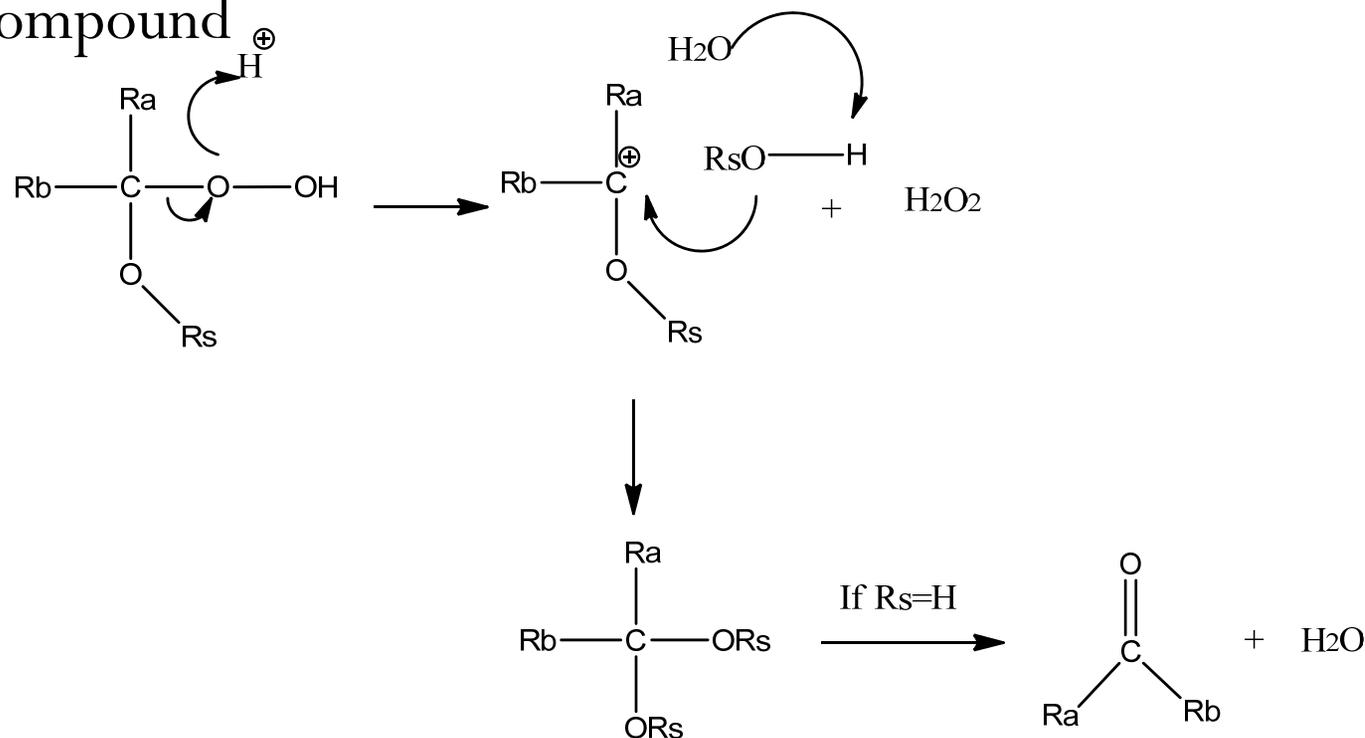
Reactions With Lignin

- Decomposition of the primary ozonide to the carbonyl and carbonyl oxide fragments is the reaction pathway that is most likely to predominate in the aqueous conditions normally used in ozone bleaching. The carbonyl oxide is trapped by water to form an a-hydroxy hydroperoxide. The fate of the hydroperoxide depends on other substituents and solvents.
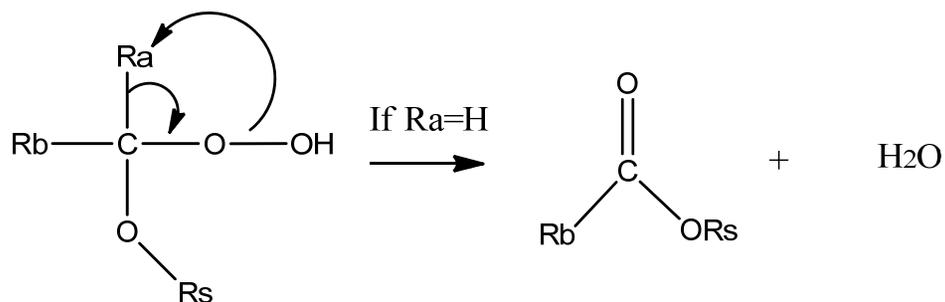
Reactions With Lignin

- Under acidic conditions, the peroxy oxygen can become protonated, forming hydrogen peroxide and a carbocation. The carbocation then reacts with water to form a gem diol that is likely to become further oxidized to a carbonyl compound

Reactions With Lignin

- Finally, if one of the groups on the hydroxy hydroperoxide carbon is hydrogen, the peroxide can decompose to water and a carboxylic acid.

$$Rb-\underset{\underset{Rs}{\overset{|}{O}}}{\overset{\overset{Ra}{|}}{C}}-O-OH \xrightarrow{\text{If Ra=H}} \underset{Rb}{\overset{O}{\overset{||}{C}}}ORs \quad + \quad H_2O$$

Reactions With Lignin

- Aromatic compounds also react by the Criegee mechanism, although at a slower rate than, alkenes. There are three sites of attack on each aromatic ring. Preferential sites of attack and higher rates of reaction will occur at those carbons with the highest electron density. Therefore, aromatic compounds with the most electron-releasing groups react most rapidly with ozone, and the ozonide forms at the carbons bearing the electron-releasing groups. Once the ring cleavage product is formed, a muconic acid, the two aliphatic double bonds also become susceptible to attack.
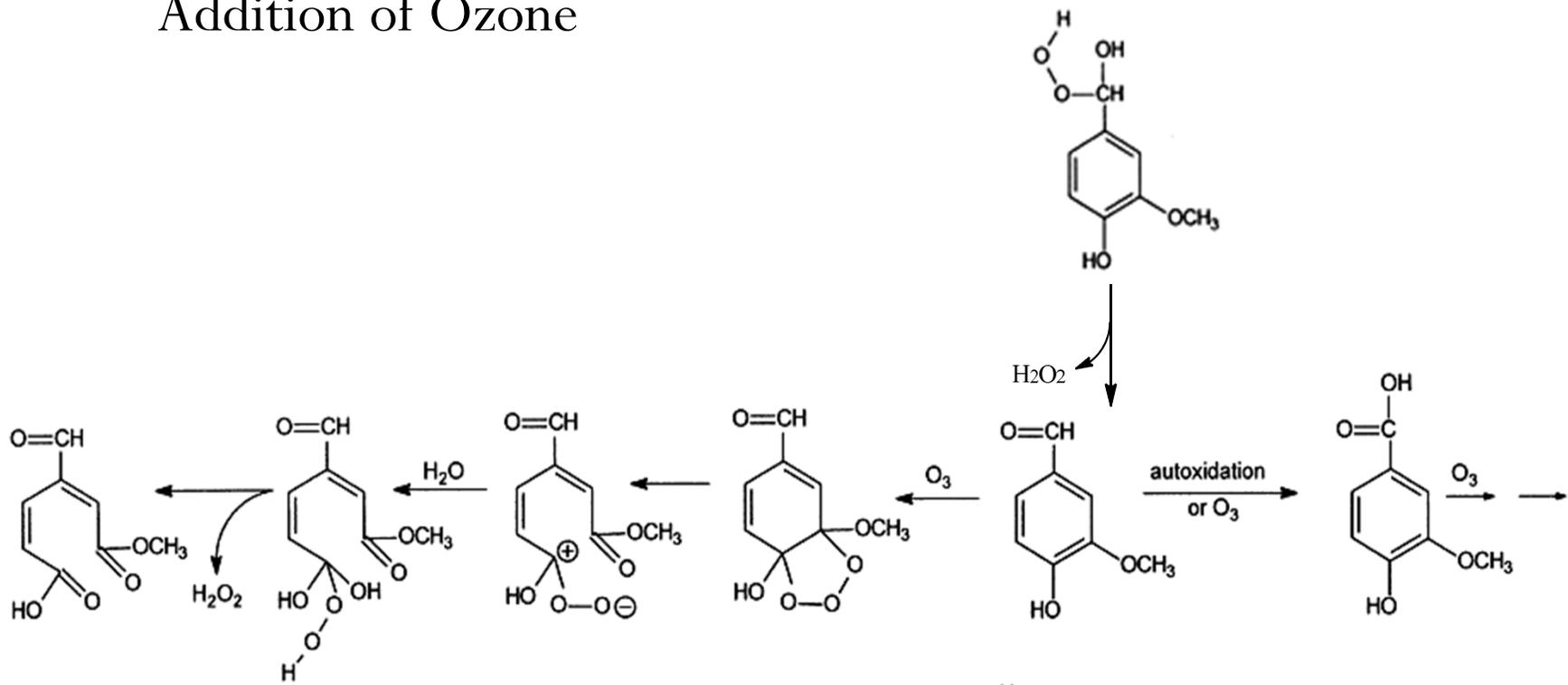
Reactions With Lignin

- Based on model compound, isolated lignin, and mechanical pulp studies, various researchers have proposed mechanisms to explain the reaction of lignin with ozone.

- Ionic Mechanisms

  Ozone Oxidation of Side-Chain Structure in Lignin via 1,3 dipolar addition mechanism
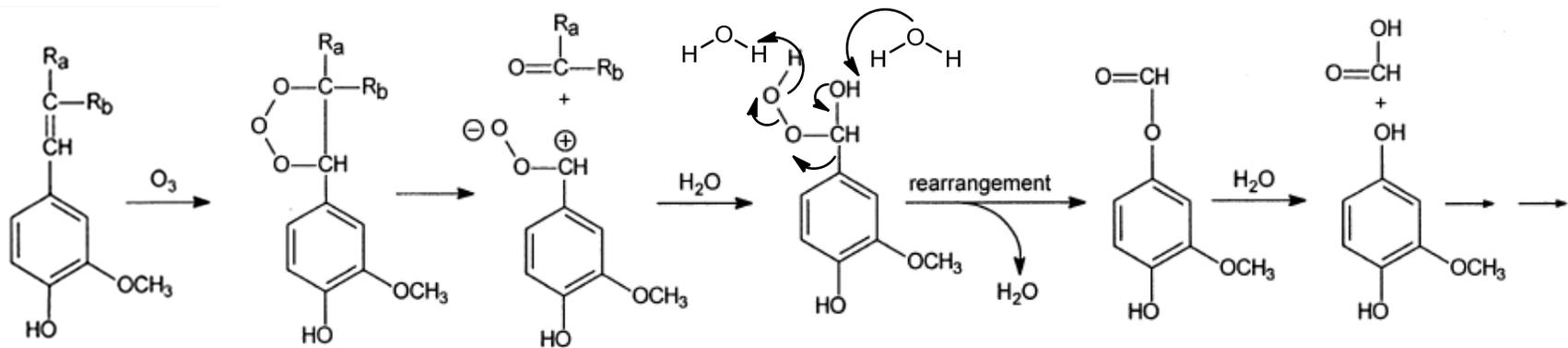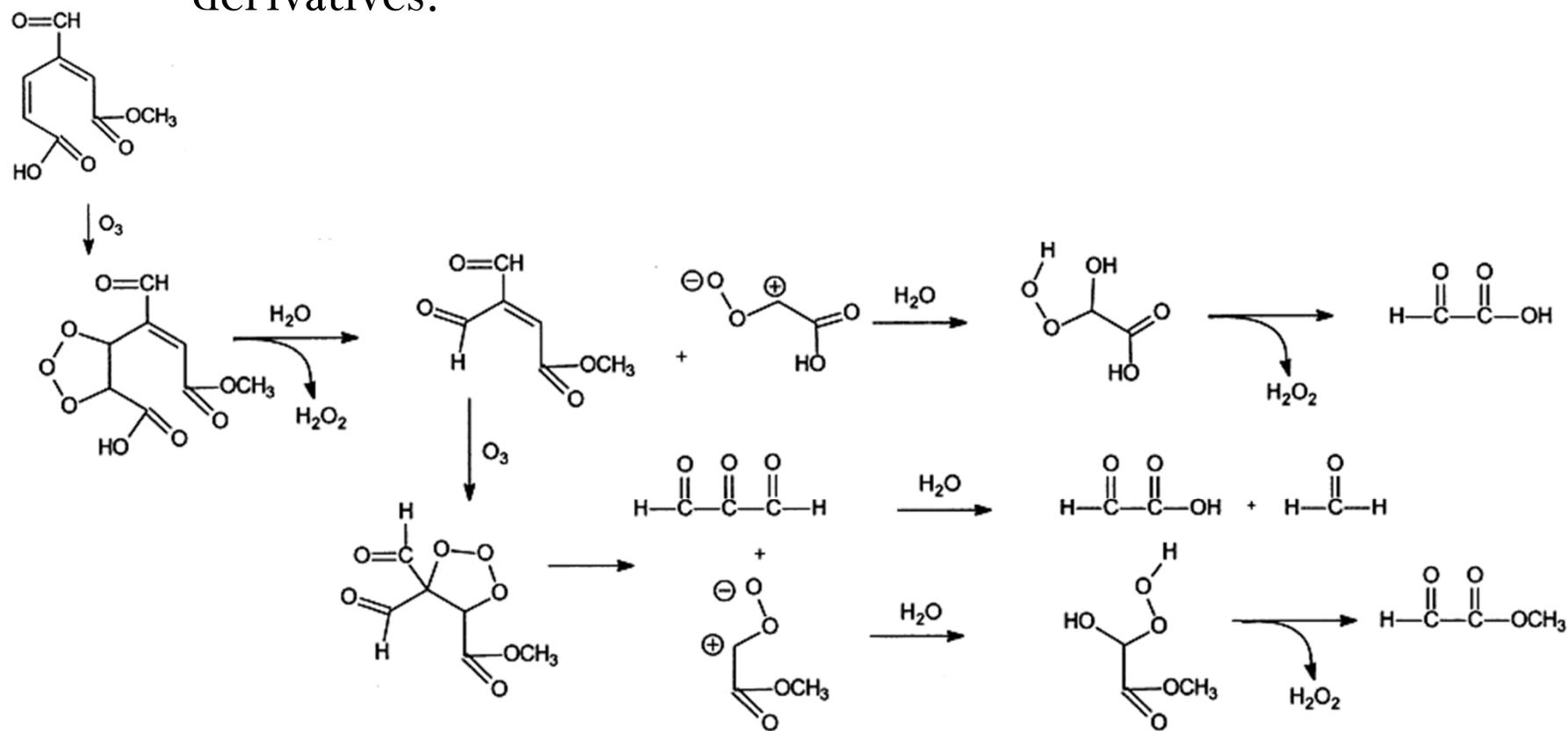
Reactions With Lignin

- Reaction of Aromatic Bonds in Lignin via 1,3 Dipolar Addition of Ozone

Reactions With Lignin

- Olefinic bonds are very labile to further attack by excess ozone. There is a mechanism for degradation of muconic acid derivatives.
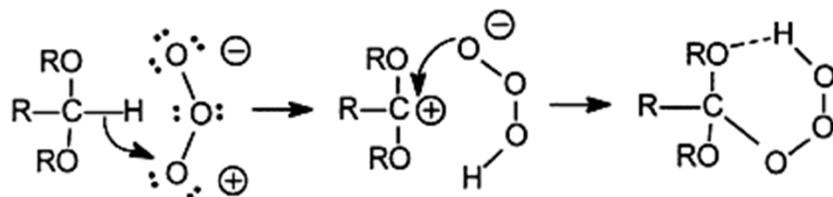
Reactions With Carbohydrates

- Carbon-hydrogen bonds in many saturated compounds are susceptible to cleavage by ozone, including the activated anomeric carbon-hydrogen bonds in carbohydrates. Highly reactive hydrotrioxide intermediates are produced from the ozonation of acetals, including glucosidic acetals. When there is an oxygen atom adjacent to the insertion site, the hydrotrioxide may be stabilized by an intramolecular hydrogen bond, forming a six-membered ring.

- Several mechanisms have been proposed for the formation of the hydrotrioxides, including
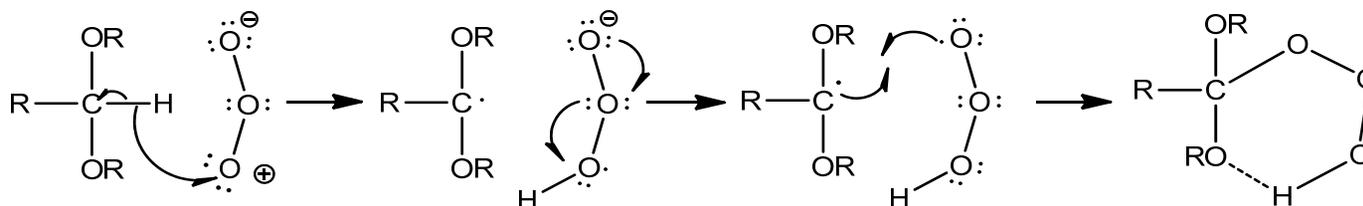
- a)1,3 Dipolar Insertion
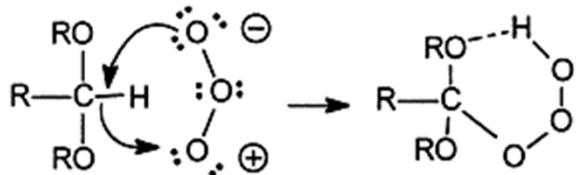
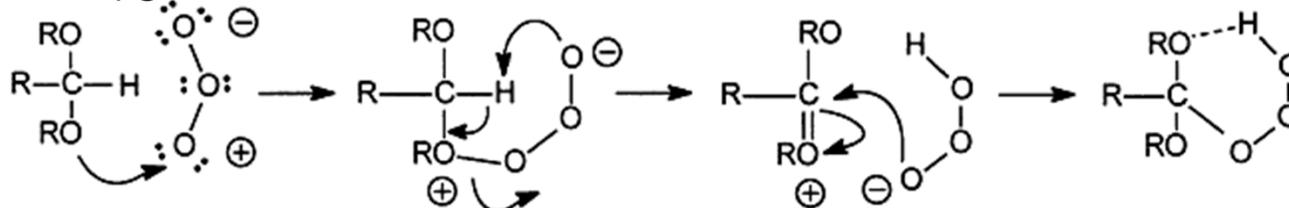# *Reactions With Carbohydrates*

- b)Hydride Transfer

- c) Hydrogen Abstraction

- d) Oxygen Attack

Most kinetic data, solvent effects, substituent effects, stoichiometry, and thermochemical calculations support either the concerted insertion,or the hydride transfer(a and b).

Reactions With Carbohydrates

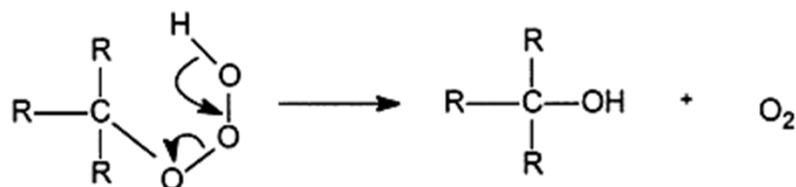- Once the hydrotrioxide intermediates are formed, they may decompose.

- The ionic decomposition pathways depend on the other substituents on the hydrotrioxide-bearing carbon, solvents, and other reactants. The products can be

- a) either carbonyls and hydrogen peroxide
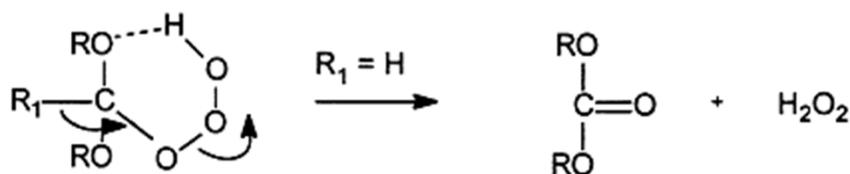
Reactions With Carbohydrates

- b) Carbonyls and oxygen

- c) Alcohols and oxygen
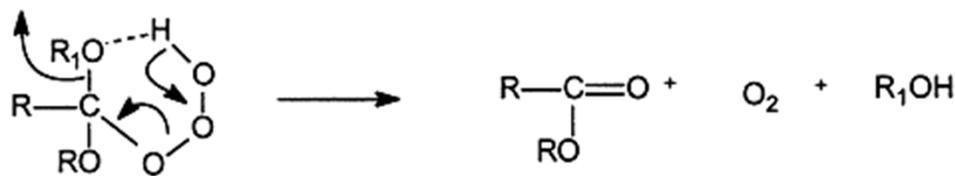
- d) Carbonyls and alkyperoxyl compounds.
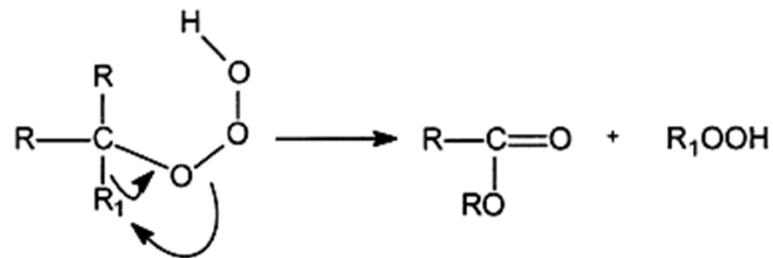
Reactions With Carbohydrates

- The major products from ozonation of aqueous solutions of 1,3-methyl glycoside are gluconolactone and gluconic acid. A decomposition pathway for the hydrotrioxide was proposed in which the glycosidic bond is cleaved, rather than the ring oxygen bond, to form gluconolactone, which subsequently hydrolyzes to form gluconic acid. These two 1,3-glycoside reaction mechanisms are illustrated at the next page.

Reactions With Carbohydrates

- Pathway b is favored.
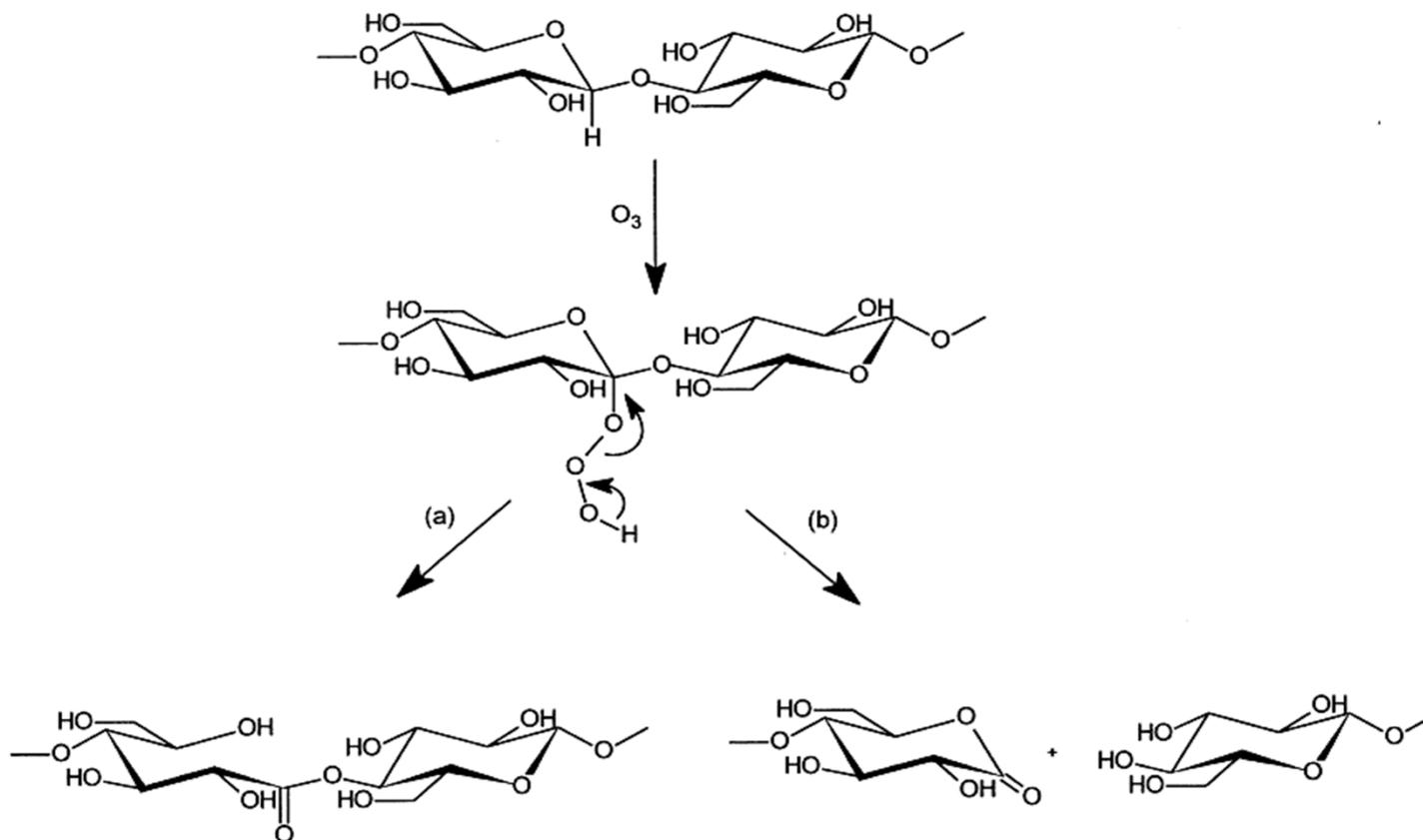
Reaction Selectivity between Lignin and Carbohydrates

- Selectivity refers to the preferential attack of a reagent on lignin versus carbohydrates. Selectivity depends, in part, on the reactivity of ozone directly with various functional groups. Second order rate constants for direct reactions of ozone with several compounds that have functional groups relevant to pulp suggest that when lignin is present, ozone should be rapidly consumed by the lignin and cellulose should be fairly unreacted.

Reaction Selectivity between Lignin and Carbohydrates

- The data suggest that carbohydrates are protected from direct reactions with ozone by the presence of lignin and lignin degradation products. Guaiacol and syringyl are nearly completely consumed before the glucoside is degraded when mixtures of the compounds are ozonated.

- The model reactivities are reflected in pulp ozonation. When initial kappa numbers of pulp are high, viscosity is retained better than when ozonation occurs in later stages of a bleaching sequence and the initial kappa numbers are low. Once a critical level of lignin has been removed from the pulp, ozone will begin to react with the C-H bonds of carbohydrates. The protecting effect of lignin appears to exist only to a point.

Effect of ozone on carbohydrates

- Formation of new functional groups in a fully bleached pulp during ozonation.

Ozone consumed, % on oven dried plup	DPv	Carboxyl content meq/100g	Carbonyl content meq/100g
0	1300	3.2	0.3
0.15	1100	3.4	0.6
0.3	910	3.5	1.2
0.85	340	3.8	1.7

- It can be seen that the ozone treatment induced the formation of carbonyl groups and to a minor extent of carboxyl groups.

Chirat, Christine; Lachenal, Dominique. Holzforschung (1994), 48(Suppl.), 133-9.

Effect of ozone on carbohydrates

- Tear index at 8 km breaking length versus DPv of ozonated pulps.
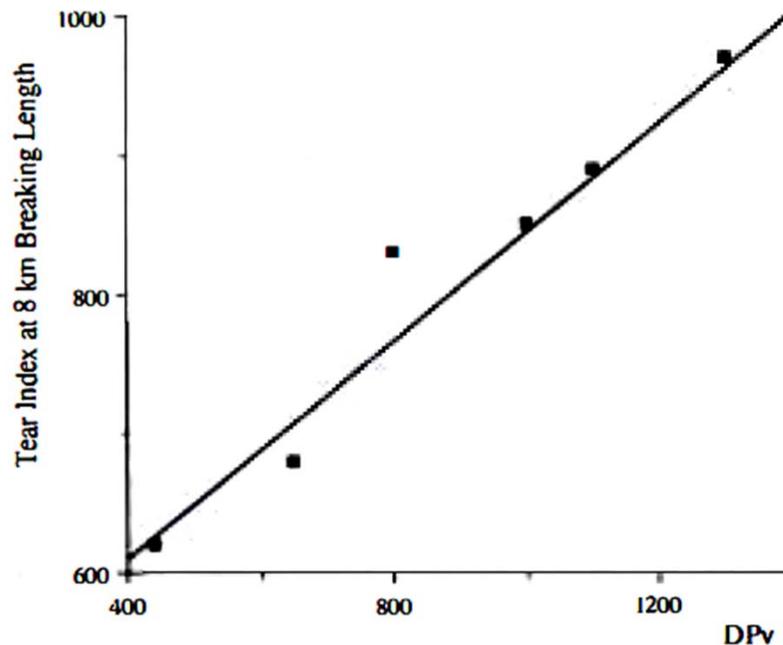
- The tear index at 8 km B. L. decreased linearly with the DPv . So the drop in DPv due to the ozone treatment induced also a drop in pulp resistance.

Chirat, Christine; Lachenal, Dominique. Holzforschung (1994), 48(Suppl.), 133-9.

Effect of ozone on carbohydrates

- Effect of an ozone treatment on the brightness stability of a fully bleached pulp

O_3 consumed%	0	0.08	0.13	0.35
ISO brightness	86.5	90.1	90.6	90.6
Drop in brightness after light exposure[1]	3.0	4.2	4.0	4.0
Idem after B[3]	2.5	2.0	2.1	2.1
Drop in brightness after heat exposure[2]	3.1	4.3	4.4	6.0
Idem after B[3]	1.9	2.3	2.5	2.3

- 1.Exposure to light: 60 min, Suntest apparatus. 2.Exposure to heat: 12 hours, 105°C, dry conditions. 3B: reductive treatment with 5 % sodium borohydride on o. d. pulp.

Chirat, Christine; Lachenal, Dominique. Holzforschung (1994), 48(Suppl.), 133-9.

Effect of ozone on carbohydrates

- The results presented in the table indicate that both heat and light induced brightness reversion were increased by the ozone treatment but the reversion upon heat exposure seemed to be more sensitive to the ozone charge. It has been shown before that ozone induced the formation of carbonyl groups on carbohydrates. The fact that the brightness stability was much better after a reductive stage carried out with sodium borohydride indicated that these carbonyl groups play an important role in brightness reversion upon heat and light exposure.

Chirat, Christine; Lachenal, Dominique. Holzforschung (1994), 48(Suppl.), 133-9.

Ozone and HexA Reactions