

Chemistry of Chlorine Dioxide Pulp Bleaching

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Bleaching History

- Bleach - *blecan* (Anglo Saxon) – to fade
- First dates back to ancient Gauls: sunlight on vegetable fibers moistened with alkaline solution from wood or vegetable ash
- Process: alkali treatment, exposure on grassy meadows to sun, washing, repeat, final treatment with lactic acid from sour milk
 - Became known as “grass bleaching”
 - Perfected around Haarlem, Holland
 - Material generally of linen fibers

Bleaching History

- 1756 – Francis Home (Scotland)
 - Discovered that by substituting dilute sulfuric acid for lactic acid in last step, operating time is reduced.
 - Still is a grass bleaching operation and not used yet for paper
 - “White” paper made from sorted white rags
- 1774 – Karl Wilhelm Scheele (Swedish Chemist)
 - discovered chlorine and pioneered use as a bleaching chemical on vegetable fibers
- Berthollet – French chemist
 - discovered chlorine could be absorbed in solution of caustic potash and resulting solution had efficient bleaching action with less degrading effect on the finished goods (product)

Bleaching History

- Thomas Henry – English
 - extended use of bleaching solution to paper (rag)
- 1798 – Charles Tennant – Scotland
 - formulated calcium hypochlorite by reaction of chlorine gas with milk of lime
- 1799 – Charles Tennant
 - patent on production of bleaching powder by action of chlorine on slaked lime – became world's most dominant bleaching agent

Bleaching History

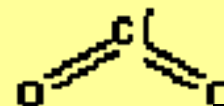
- 1920's: Continuous operating bleaching introduced by Thorne in multi-stage bleaching
 - for purification of pulp from demand for large tonnages of nitrocellulose during WWI
 - 2 stage hypochlorite then added alkaline extraction in between hypochlorite stages
- Use of Chlorine dioxide investigated from 1920 – 1940, put into production 1940's

Chlorine Dioxide History

- 1946 – 1980's used as a later bleaching stage, not for delignification
 - CEHDED, CEDED
- Late 1980's realized that ClO_2 and Cl_2 used together had a higher delignification efficiency than Cl_2 alone
- Environmental regulations dictated the switch from elemental chlorine (Cl_2 & HOCl) to ClO_2 and other TCF methods

Chlorine Dioxide

- Molecular Weight: 67.45
- Boiling Point: 11°C
- Yellow green to orange gas, with a sharp pungent odor
- Water soluble, 10 g/L
- Oxidant
- Density: 2.4 x's water
- Decomposes to Cl₂ and O₂ with noise, heat, flame, and minor pressure wave

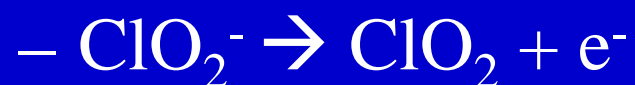


Formation of Chlorine Dioxide

- Reduction of chlorate in acidic medium:



- Oxidation of chlorite ion:



Reductive Chemistry

- Reducing agents are used to make the e^-
 - $\text{SO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 4 \text{H}^+ + 2 e^-$
 - $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + 4 \text{H}^+ + 4 e^-$
 - $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + e^-$
 - $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}^+ + 2 e^-$

Making Chlorine Dioxide

- $2 \text{ClO}_3^- + \text{SO}_2 \rightarrow 2 \text{ClO}_2 + \text{SO}_4^{2-}$
- $4 \text{ClO}_3^- + \text{CH}_3\text{OH} + 4 \text{H}^+ \rightarrow 4 \text{ClO}_2 + \text{HCOOH} + 3 \text{H}_2\text{O}$
- $\text{ClO}_3^- + \text{Cl}^- + 2 \text{H}^+ \rightarrow \text{ClO}_2 + \text{Cl}_2 + \text{H}_2\text{O}$
- $2 \text{ClO}_3^- + \text{H}_2\text{O}_2 + 2 \text{H}^+ \rightarrow 2 \text{ClO}_2 + \text{O}_2 + 2 \text{H}_2\text{O}$
- $\text{ClO}_3^- + 6 \text{H}^+ + 6\text{e}^- \rightarrow \text{Cl}^- + 3 \text{H}_2\text{O}$

Chlorine Dioxide

Chemical properties:

One of several known oxides of chlorine.

Chlorine dioxide is a powerful oxidizing agent - an electron receiver. This means that the chlorine dioxide molecule is in constant search for an additional electron. → **Disinfection** The destruction of pathogenic and other kinds of microorganisms by physical or chemical means

When a bacterial cell comes into contact with chlorine dioxide it donates an electron from its cell wall, thereby creating a breach in the cell wall through which cell contents pass in an attempt to bring the concentrations on either side of the cell membrane to equilibrium. The cell dies through lysis.

Chlorine Dioxide

How long has chlorine dioxide been used?

Chlorine dioxide has found widespread use since the early 1950s in the treatment of drinking water and swimming pools.



Today, chlorine dioxide is used by many large cities in Europe, such as (1956) Brussels, Zurich, Düsseldorf, Toulouse and Vienna, to sanitize the drinking water supply.



Chlorine Dioxide

Chlorine dioxide has many applications:

- **Food industry**
Fruit and vegetable washing
Meat and poultry disinfection
Sanitizing food process equipment
- **Medical**
“Tristel” sterilizing solutions for medical instruments
Air disinfection and building decontamination.
(2001 anthrax attacks, US)
- **Personal hygiene**
Mouthwashes (~0.003%)
Toothpastes
Contact lens cleaners
- **Other industry**
Cooling systems and towers in the control of
Legionella.(Gram negative bacterium)



Bleaching Pulp with Chlorine Dioxide

Advantages

- High brightness and brightness stability
- Excellent for shive and dirt removal - the best
- Highly selective - little degradation of pulp
- Less organic chlorine than Cl_2 and ClO^-
- Radical scavenger

Bleaching Pulp with Chlorine Dioxide

Disadvantages

- **Highly explosive – hence generate on-site**
- **Highly corrosive - need titanium equipment - high capital cost**
- **Expensive**
- **Toxic - handle with care**
- **AOX**
- **Chlorate formation**
 - **26-40% loss in oxidation power**

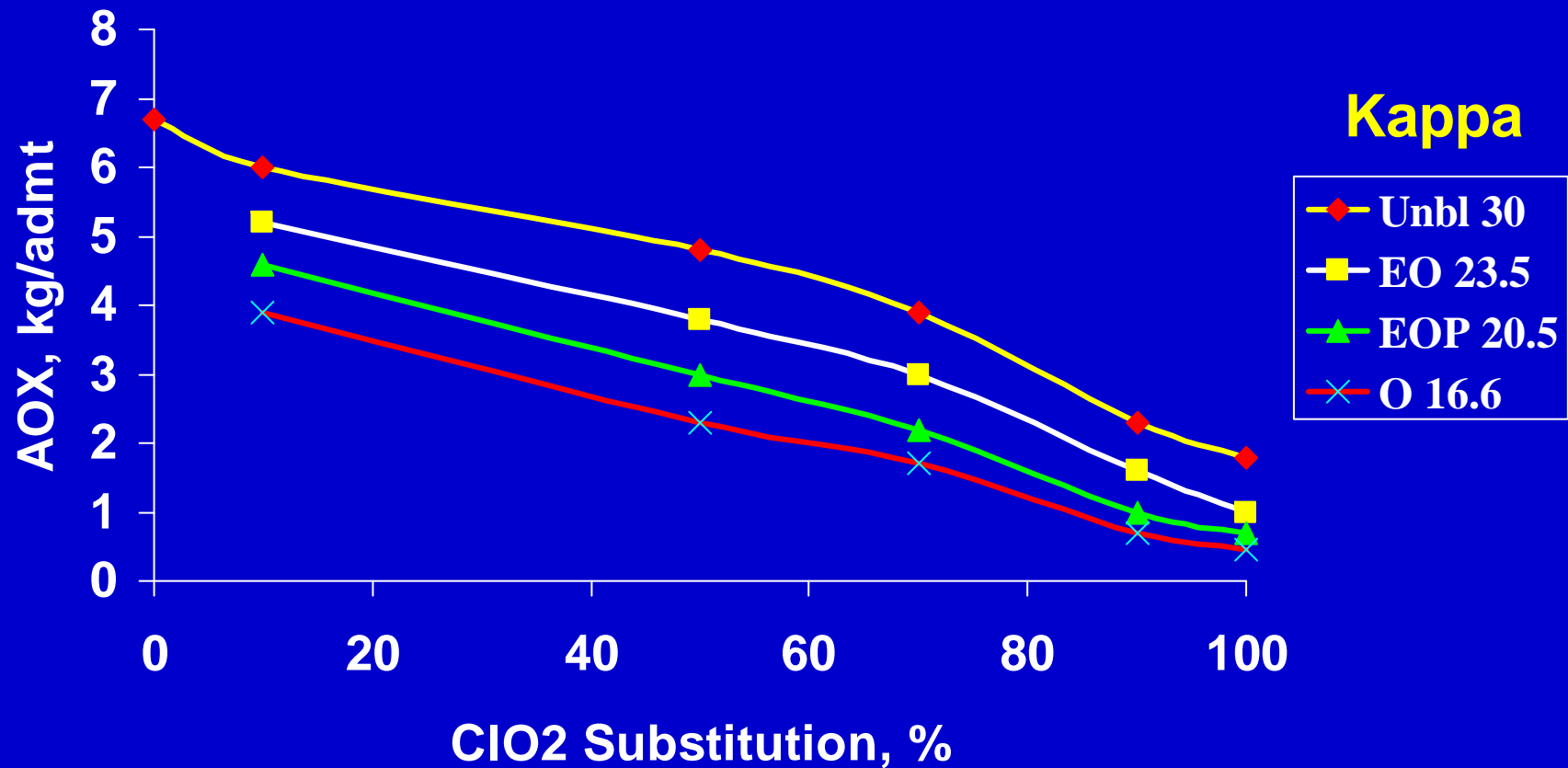
ClO₂ Delignification Process Conditions

- Total Chemical Charge: 0.15 – 0.25 kappa factor
- Chlorine dioxide charge: 25 – 100% of the total
- Temperature: 30 -60° C
- Total Time: 20 – 60 minutes
- End pH: 1.5 – 3
- Consistency: 3 – 4%

Chlorine Dioxide Puffs

- Puff – decomposition of chlorine dioxide
 - $2 \text{ClO}_2 \rightarrow \text{Cl}_2 + 2 \text{O}_2 + \text{heat}$
 - Low speed wave of reaction ($< 1 \text{m/s}$)
 - Explosion: $> 300 \text{ m/s}$
 - Generators designed for up to 200 mm Hg

AOX vs. ClO₂ Substitution



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Substitution of Chlorine Dioxide

- AOX Generation

- $\text{AOX (kg/t)} = 0.1 (\text{Cl}_2, \text{kg/t active chemical})$

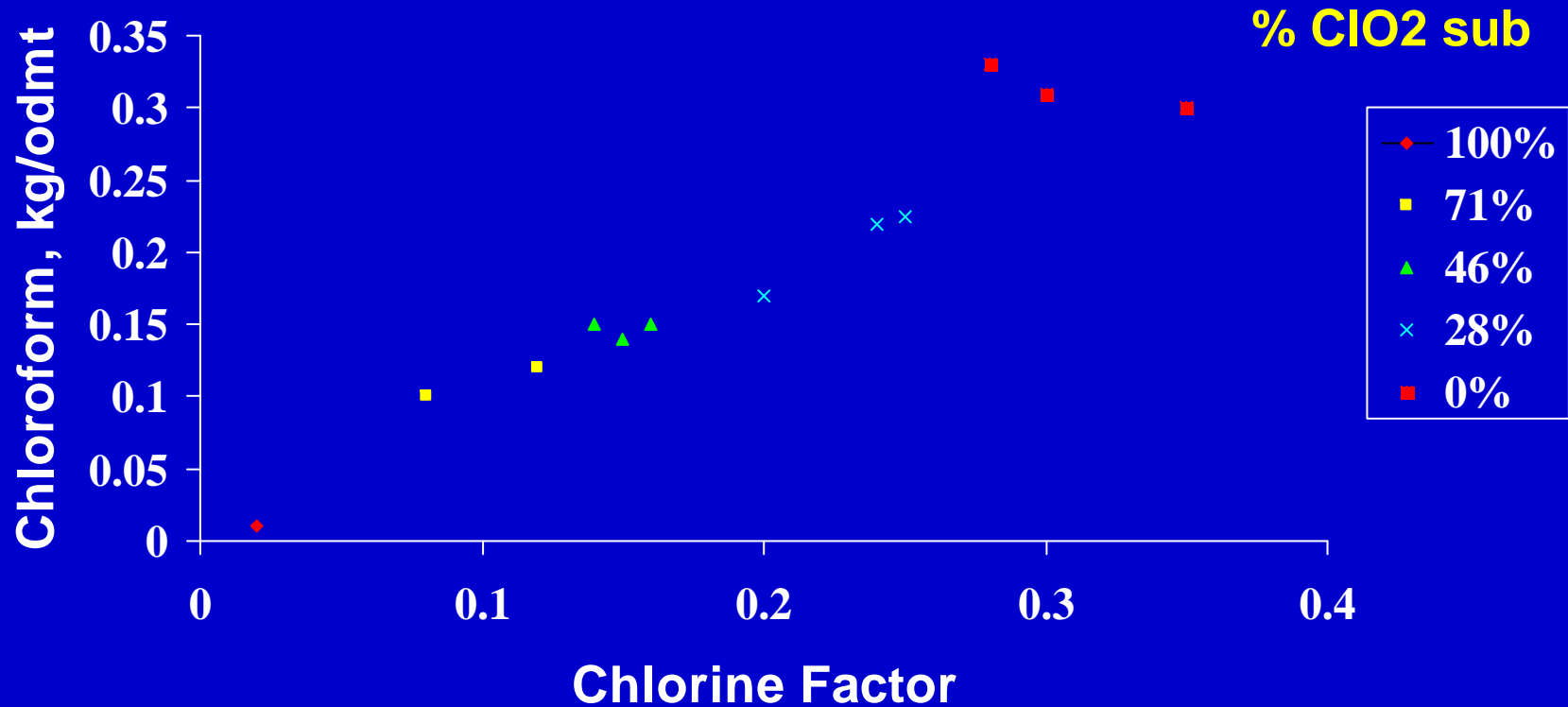
- $\text{AOX (kg/t)} = 0.1(1/2.63)(.526)(\text{ClO}_2, \text{kg/t active chemical})$
 $0.02(\text{ClO}_2, \text{kg/t act chemical})$

- On an equal weight basis ClO_2 is 2.63 times as reactive as Cl_2

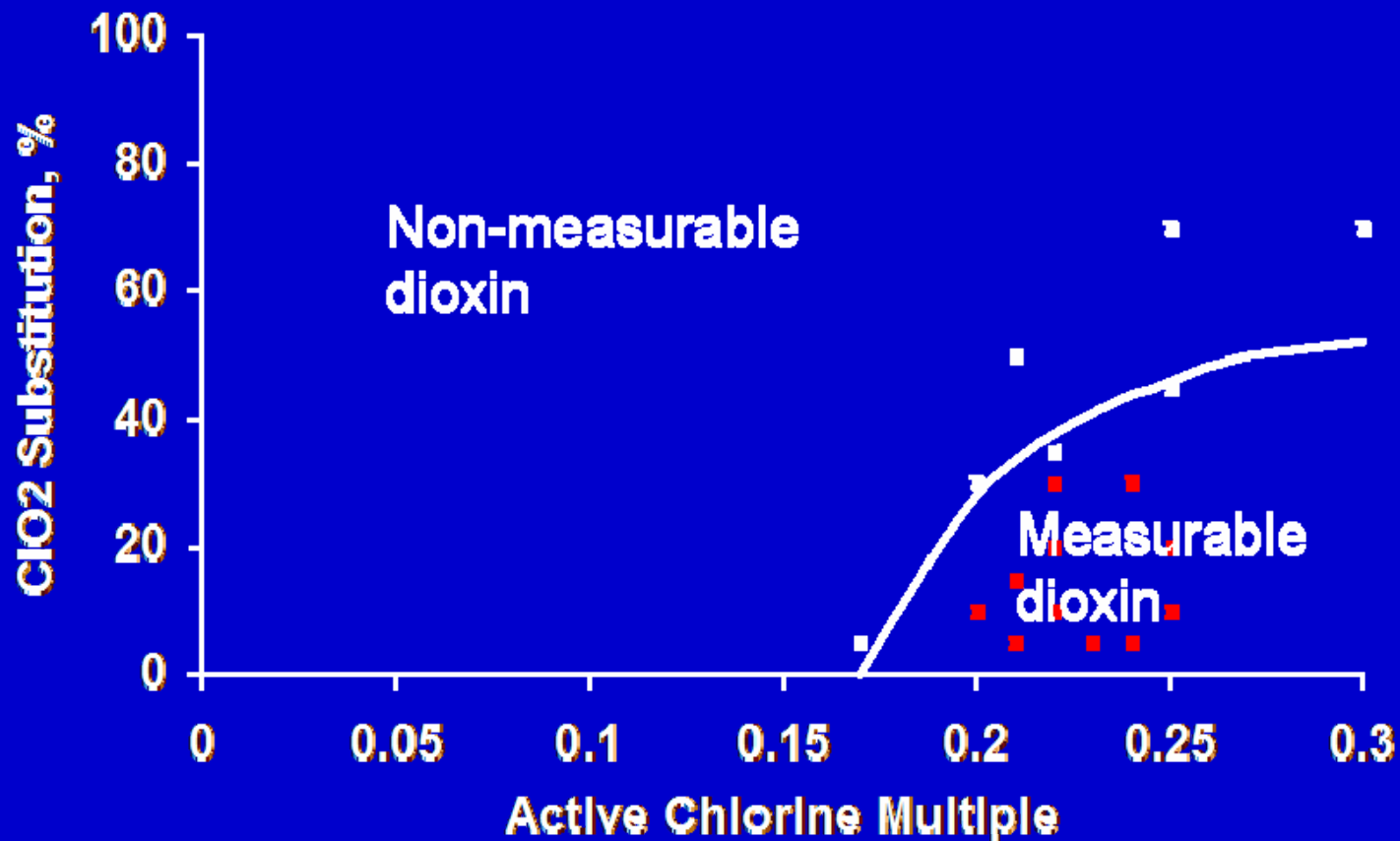


$$35.5 / 13.5 = 2.63$$

Chloroform – CHCl₃



Effect of Chlorine Multiple on Dioxin Formation



Substitution of Chlorine Dioxide for Chlorine

Old Bleaching Sequences:



ECF Sequences:



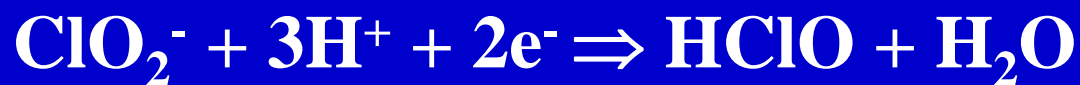
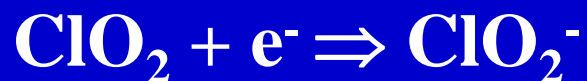
ECF = Elemental Chlorine-Free

Chlorine Dioxide



Chlorine Dioxide

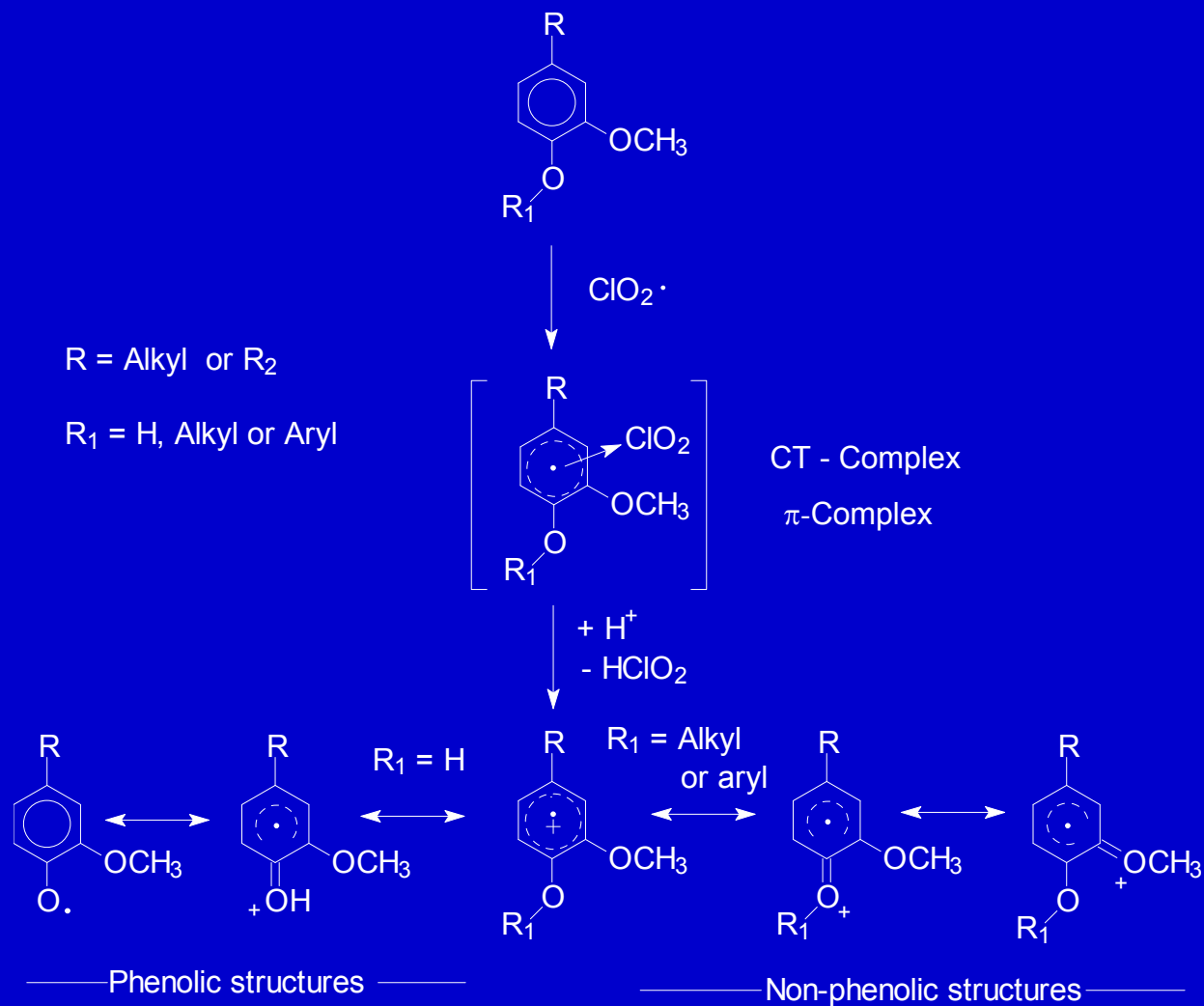
- Chemistry



Equivalent Weight: $\text{ClO}_2 = 67.5/5 = 13.5$

$\text{Cl}_2 = 71/2 = 35.5$

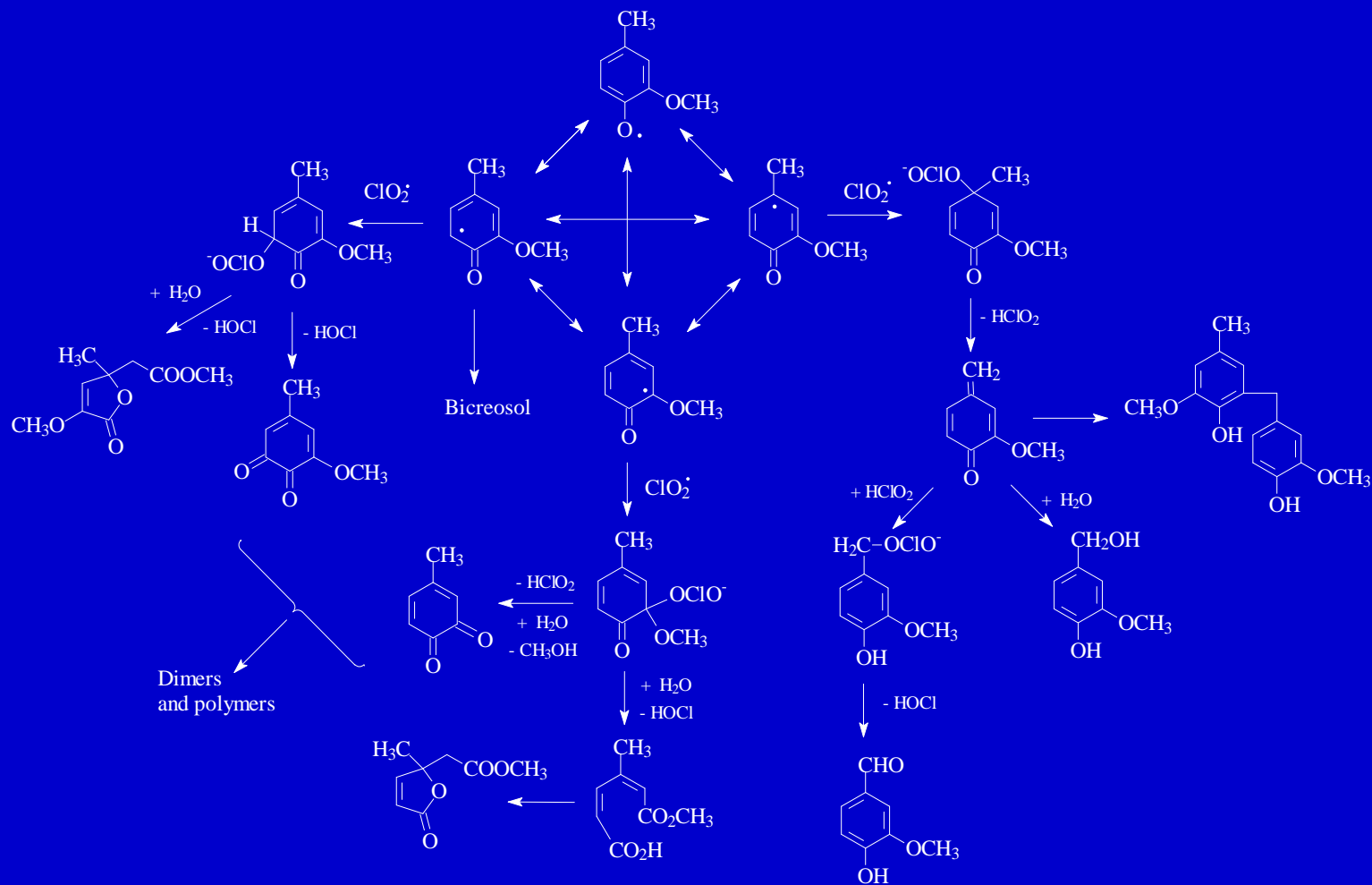
Basic Cation Radical Mechanism of Chlorine Dioxide



Brage, Ericksson and Gierer, Holzforschung, 45(1):23 (1991)

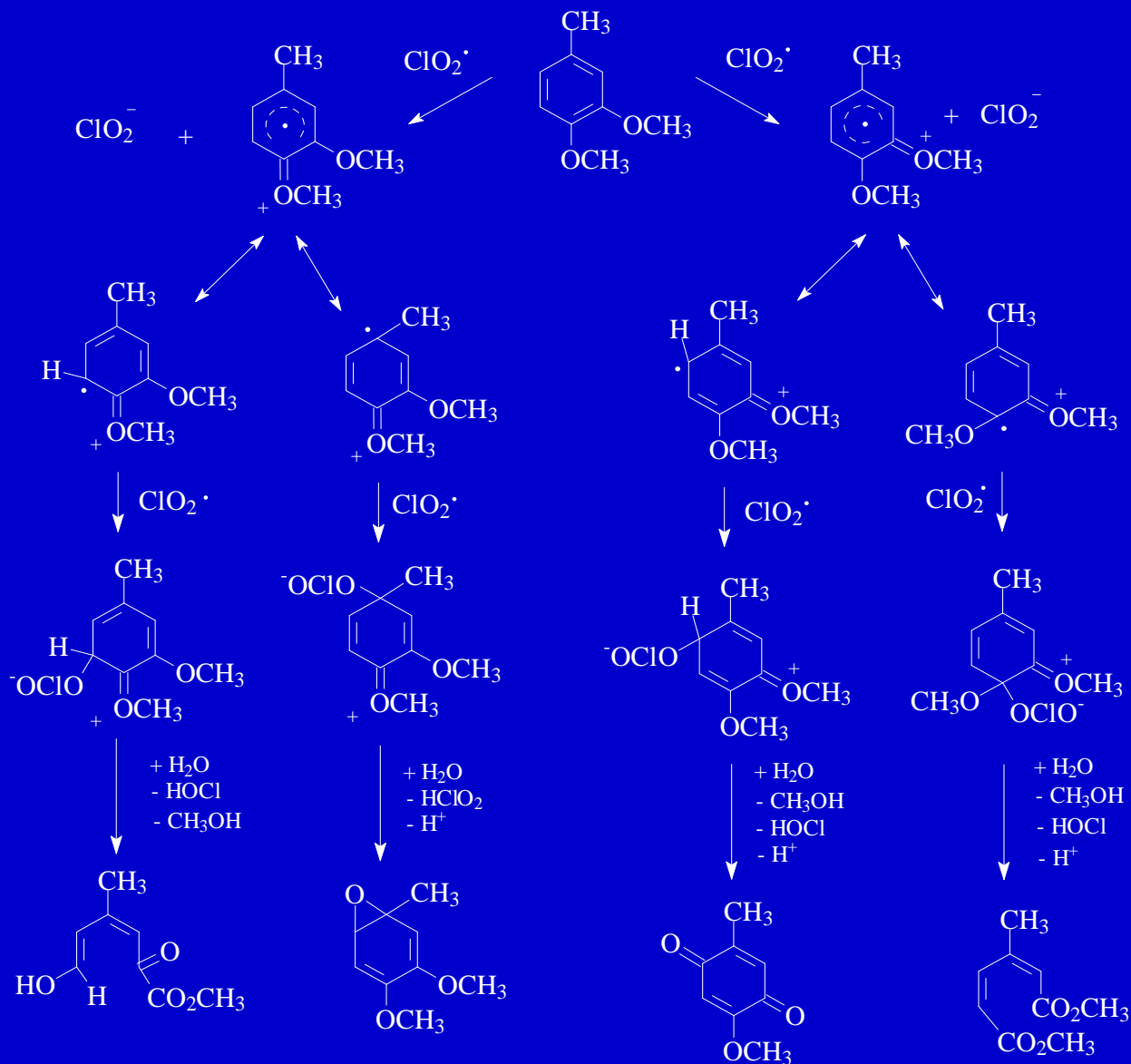
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Basic Phenolic Compound Reactions



Brage, Ericksson and Gierer, Holzforschung, 45(1):23 (1991)

Basic Non-Phenolic Compound Reactions

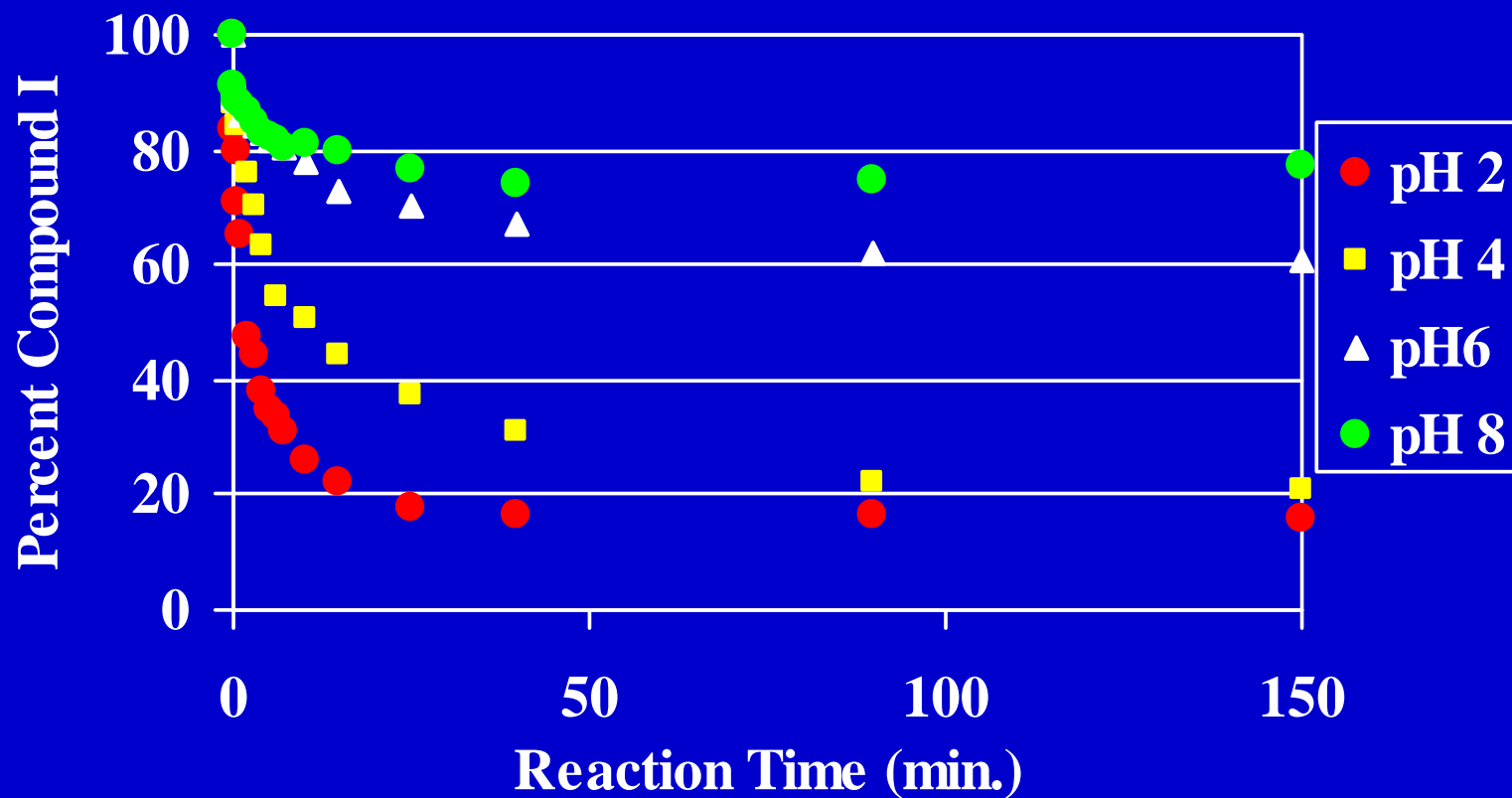


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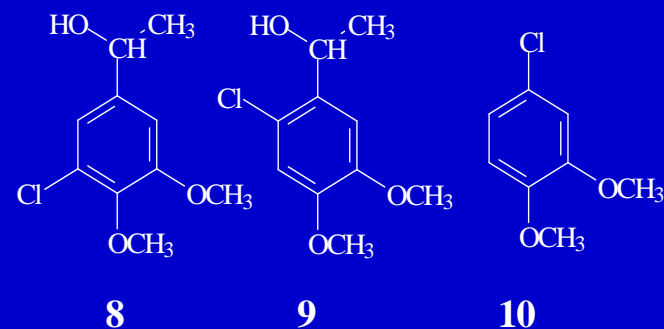
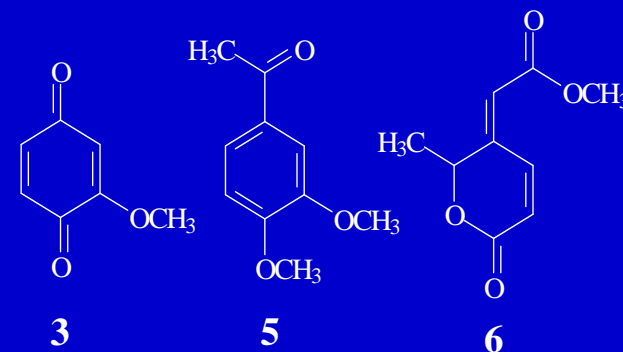
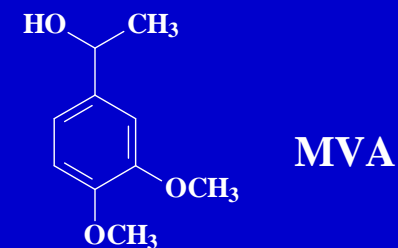
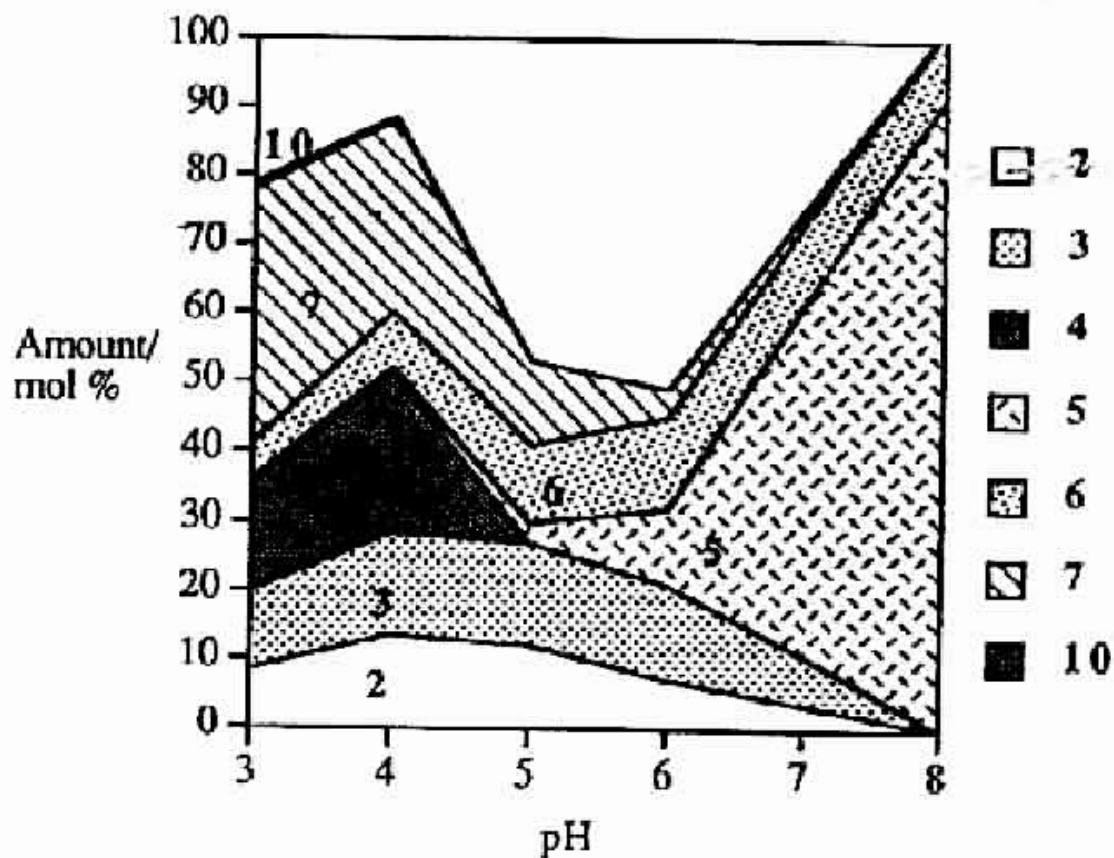
Brage, Ericksson and Gierer, *Holzforschung*, 45(1):23 (1991)

ClO₂ Oxidation of Methylveratryl Alcohol

Effect of pH on Rate of Reaction



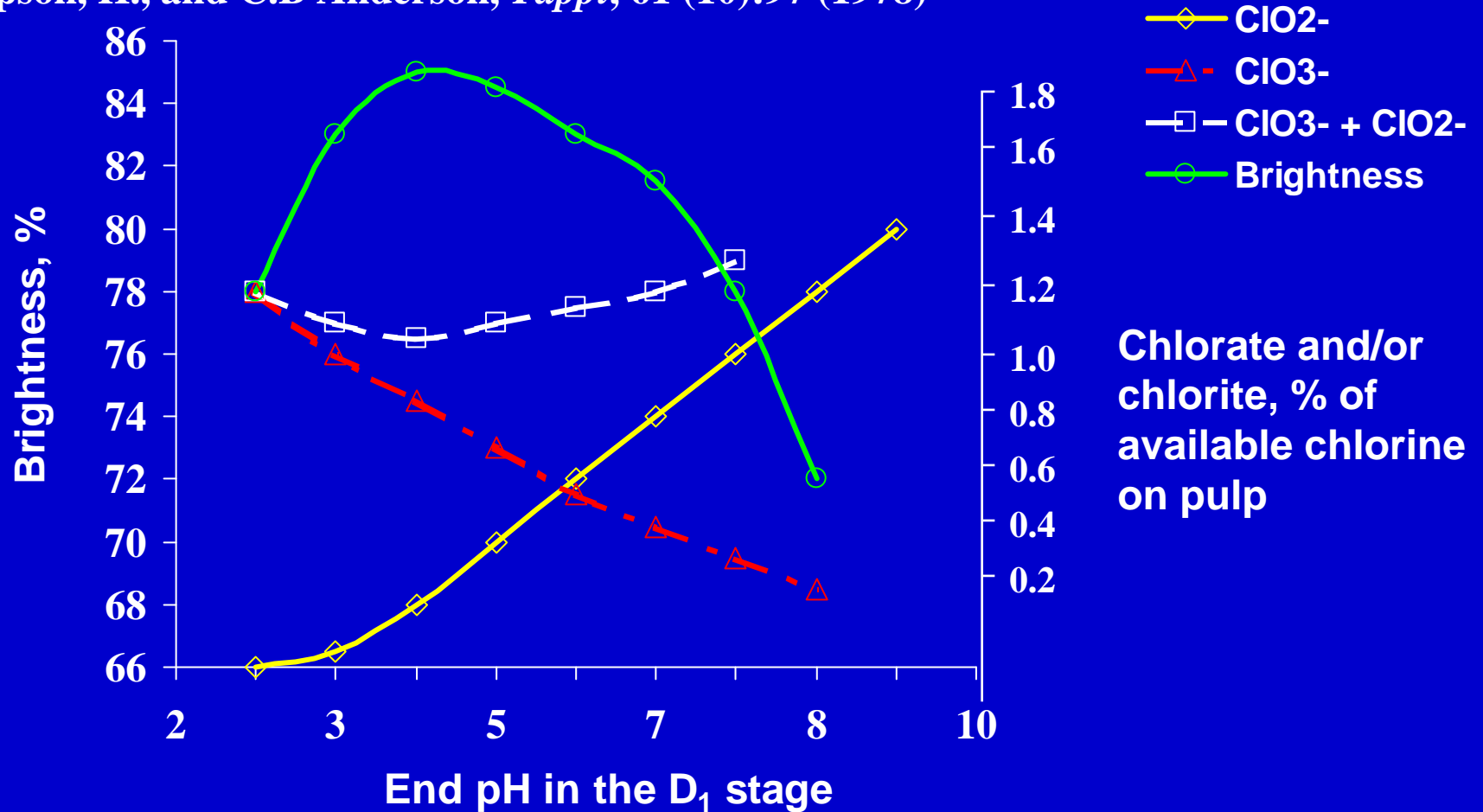
Effect of pH on the Reaction of ClO₂ with Methylveratryl alcohol (MVA)



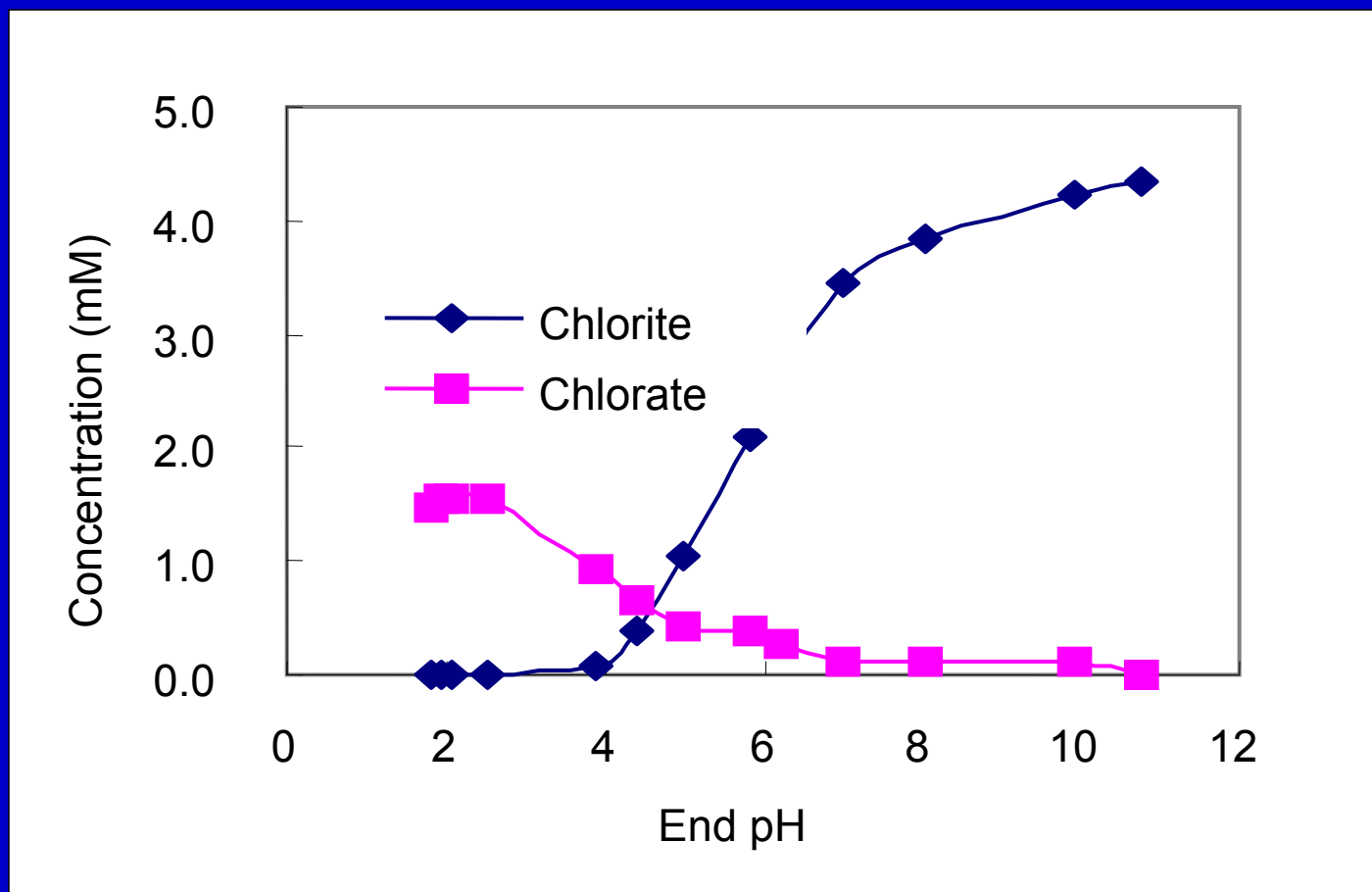
Gunnarsson and Ljunggren, *Acta Chem. Scand.*, 50: 442 (1996)

Effect of End pH in a D₁ Stage on Brightness and Chlorite and Chlorate Formation

Rapson, H., and C.B Anderson, *Tappi*, 61 (10):97 (1978)



Effect of pH on ClO_3^- and ClO_2^- formation in ClO_2 prebleaching of oxygen delignified kraft pulp

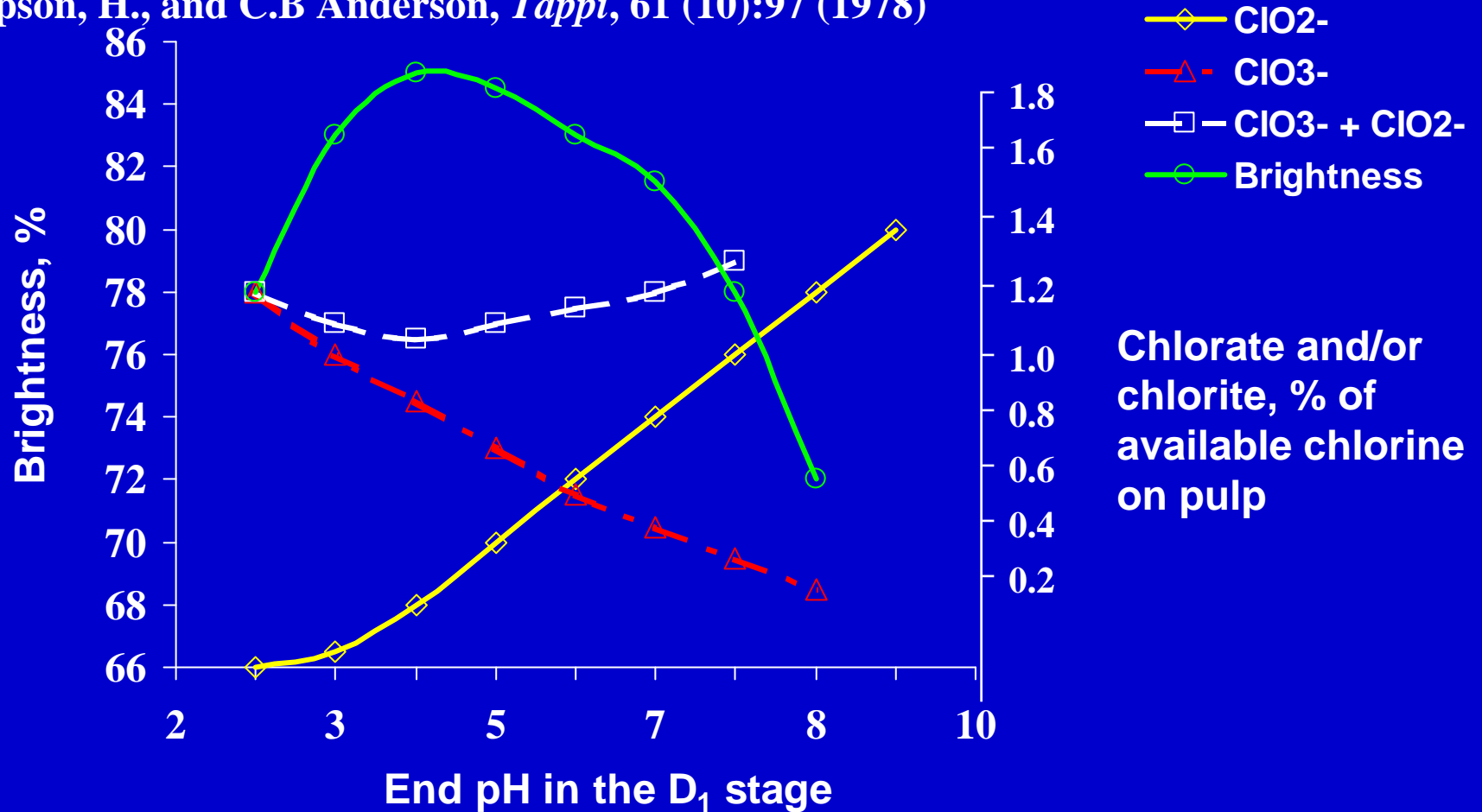


Kappa no. 10.7, kappa factor 0.20, pulp consistency, 3.5%, 60°C, 60 min

Wang, L. J. and B. H. Yoon, Paper presented at the International symposium on Cellulose and Lignocellulosics Chemistry 2000, Dec. 16-18, 2000, Kunming, China

Effect of End pH in a D₁ Stage on Brightness and Chlorite and Chlorate Formation

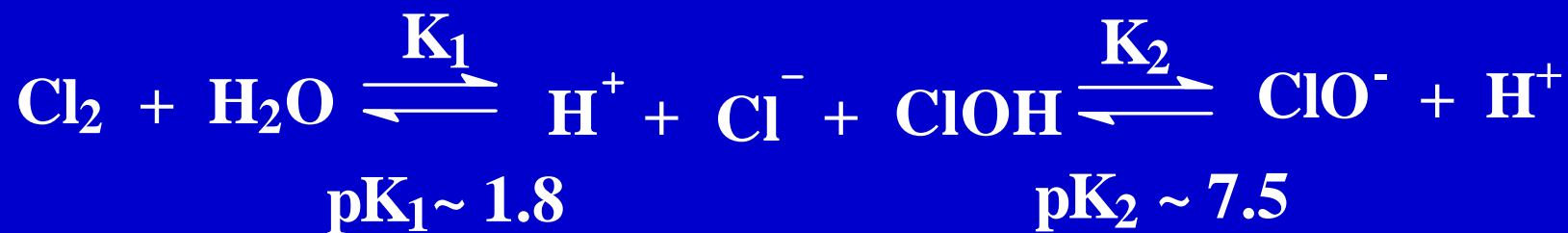
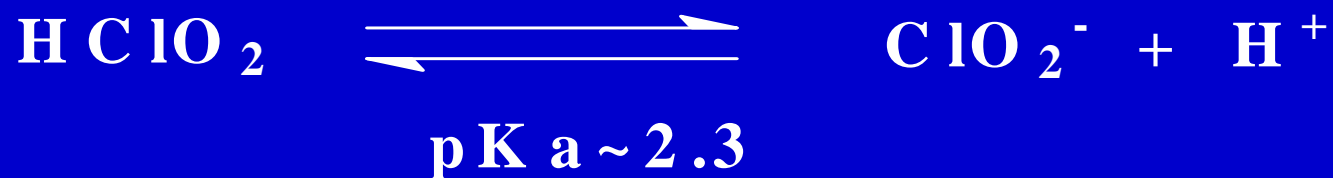
Rapson, H., and C.B Anderson, *Tappi*, 61 (10):97 (1978)



Chlorate Forming Reactions



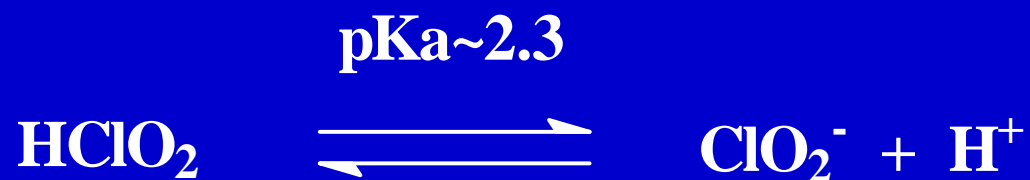
Dissociation Constants of Hypochlorous and Chlorous acids



Disproportionation of Chlorous Acid



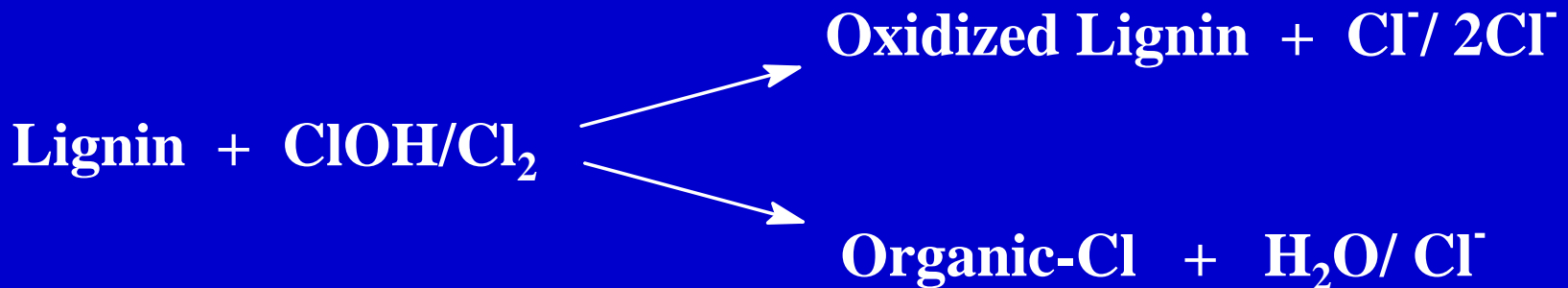
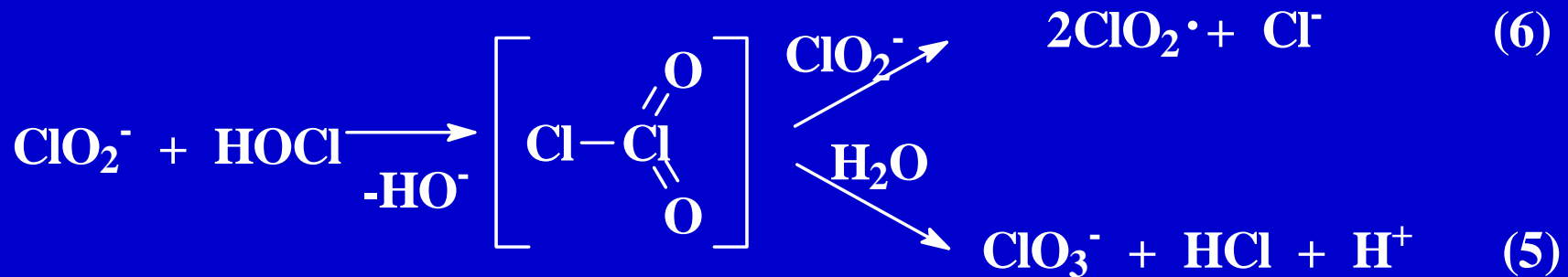
$$-\text{d}(\text{ClO}_2^-)/\text{dt} = k_1(\text{HClO}_2)^2 + k_2(\text{ClO}_2^-)(\text{HClO}_2)$$



Kieffer and Gordon, *Inorganic Chem.*, 7(2):239 (1968)

Hong and Rapson, *Canadian J. Chem.*, 46:2053 (1968)

Competitive Reactions of Hypochlorous Acid



Summary

- In D_0 , the increase in chlorate and bleaching efficiency levels off at end pH below 3.4, whereas AOX continues to increase with decreasing pH.
- In D_0 , the phenolic hydroxyl content of lignin in pulp has little effect on either chlorate formation or bleaching efficiency.

Summary

- The phenolic lignin structures have demonstrated enhanced reactivity with chlorine dioxide over that of the non-phenolic units.
- The initial stage of ClO_2 delignification is believed to be the abstraction of an electron from the phenolate anion followed by further degradation caused by additional equivalents of chlorine dioxide.
- Lactones, muconic acid esters, maleic acid, oxiranes and quinoid structures are the dominant oxidation products along with significant levels of methanol.
- Chlorinated organics are produced during ClO_2 bleaching, primarily due to the *in situ* formation of hypochlorous acid.



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