Reaching for Control of Oxygen's Effects

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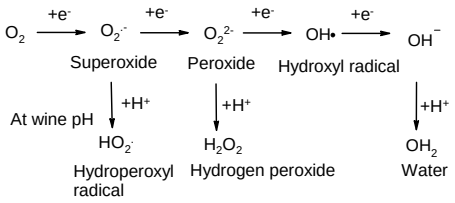
or How Terroir Could Affect Aging?

These results will soon appear in:
1) American Journal of Enolgy and Viticulture as a review and theory of wine oxidation, and
2) Journal of Ag and Food Chemistry, on the test of glycerol oxidation
Additional studies will be coming soon

Plan

- Oxygen basics
  - Theory of wine oxidation
- Test of theory
  - Glycerol oxidation
  - Importance?
- Implications in winemaking

Oxygen Reduction Cascade



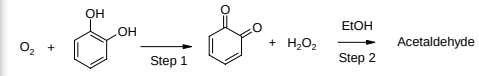
Fenton Reaction

Ferrous iron → Ferric iron

$Fe^{(II)} + HO{-}OH \longrightarrow Fe^{(III)} + OH\bullet$

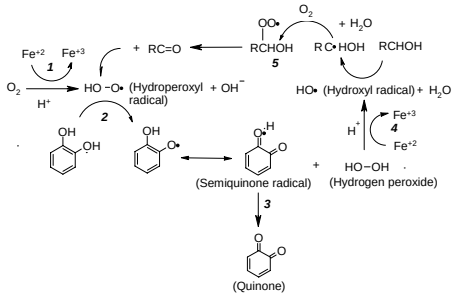
Hydrogen peroxide → Hydroxyl radical

"Well Accepted" Oxidation Steps



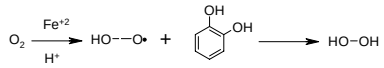
- Oxygen reacts with phenols to yield quinone and hydrogen peroxide
- Hydrogen peroxide oxidizes ethanol to acetaldehyde

Oxygen Reduction in Wine

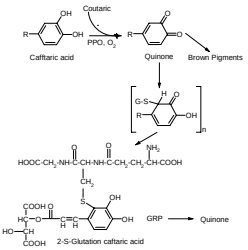


Polyphenols are Pro-oxidants

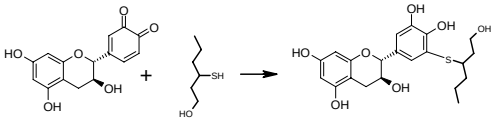
- Generation of hydrogen peroxide from dioxygen
- They are H· donors

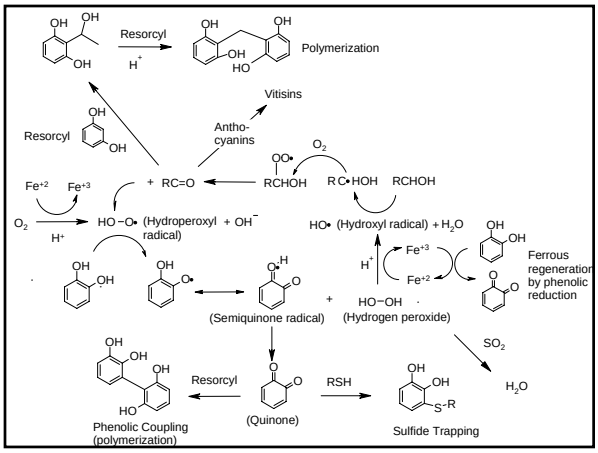


Quinone + Thiols (mercaptan)

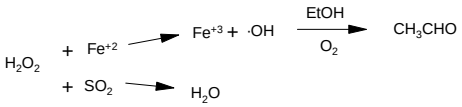


Catechin + 3MH





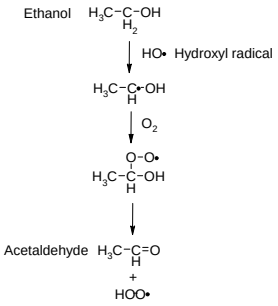
Peroxide Competition



Reactivity of Hydroxyl Radical

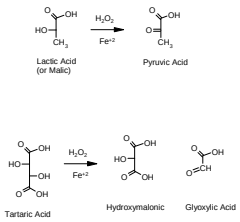
- Extremely reactive
  - Oxidizes the “first” molecule it encounters
- Oxidation products are determined by concentration
- Antioxidants cannot protect against this oxidation
- Can glycerol be oxidized?
  - Major component 0.5-0.8%
- Can acids or sugars also be oxidized?

Ethanol to Acetaldehyde



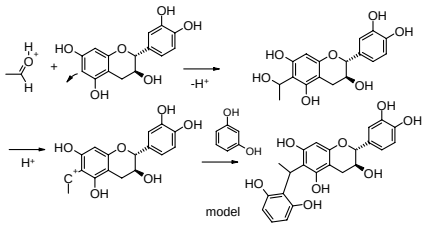
Oxidation of Wine Acids (Alcohols) to Carbonyls

- Pyruvic
  - Observed in wine
  - Reacts with anthocyanins to make wine pigments
- Glyoxylic
  - Observed in wine
  - Condenses with flavan-3-ols



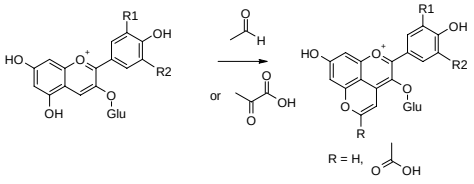
Aldehyde Coupling of Phenolics

- Importance of aldehydes in tannin coupling



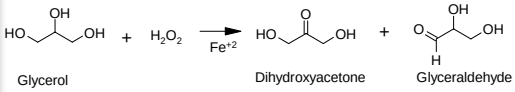
Wine Pigment Reactions

- “D-ring” formation by acetaldehyde and pyruvate



Glycerol Oxidation

- Two novel oxidation products
- Not previously reported in wine
  - Can they affect wine color, etc?
  - They do slightly darken red wine when added



Laurie and Waterhouse, Journal of Agricultural and Food Chemistry, May 2006

Oxidation in Winemaking

- Above diagrams and the following "advice" are based on our new theory!!!
  - The glycerol test only "proved" a small piece of the puzzle
- Important components to measure
  - Oxygen
  - Phenolics
  - Iron and (copper?)
    - Copper is reported to participate in the Fenton reaction
  - SO_2
  - Other redox active compounds (ascorbate)

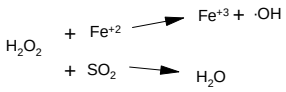
Oxygen Measurement

- Important levels?
  - Standard meter
    - Limit of Detection ~0.5 ppm
  - Orbisphere or other expensive meter
    - LOD ~2 ppb

Other Measures

- Phenolics
  - Folin OK
- Iron and copper
  - ppm by AA
    - (check with Barry Gump for the proper standardization technique)
    - If iron in wine is from the soil, then could differential amounts in soil affect aging? (Is this a chemical explanation for Terroir?!!)
- SO_2
  - Usual methods

Planned Experiments



- Effect of phenolics on regenerating ferrous iron
- Other Fenton products?
  - Sugars, acids, alcohols
- Effect on color, etc
- Dioxygen reaction?

Acknowledgements

- V. Felipe Laurie
  - Chilean graduate student, returning to Chile this fall, will work at Univ Talca
- John Daniliewicz
  - Retired Pfizer chemist in UK
- Many, many others
  - Fenton, Singleton, Cheynier, etc
- California Competitive Grant Program for Research in Viticulture and Enology
- American Vineyard Foundation

Please Let Me Know if You Have Questions

- Oxidation, Phenolics, Chemistry
- Current issues/problems
- Would an industry-wide survey be useful?
  - Staffing needs
  - Current lab procedures
  - Current production practices
    - What else would be helpful?