



The Kinetics of Oxygen Uptake by Iron in Wine-Like Solutions

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Abstract

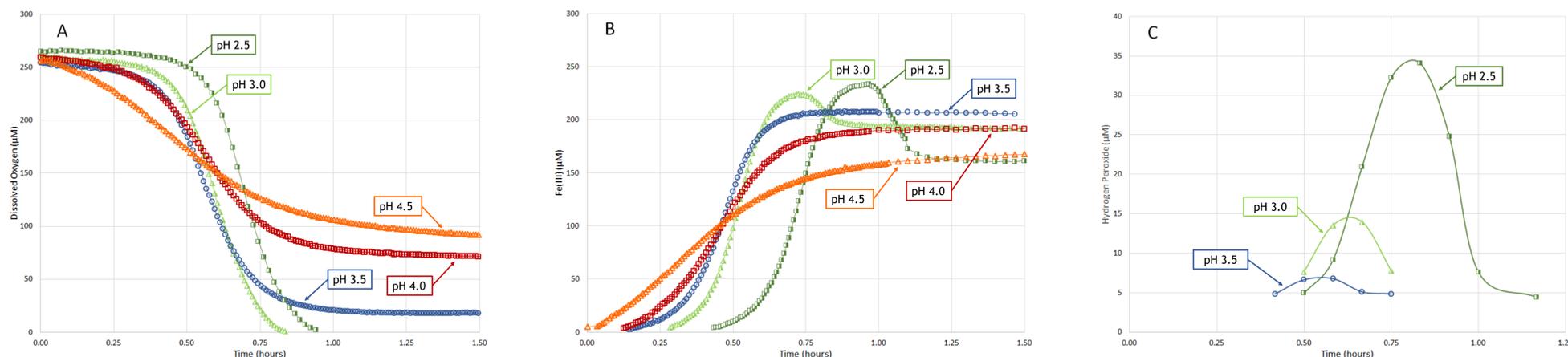
Iron mediated catalysis of dioxygen in tartaric acid solution sets the basis for wine oxidation studies. The speciation of Fe(II) and Fe(III) changes significantly over the pH range of wine. This work follows the autocatalytic nature of both dissolved oxygen consumption and Fe(III) formation kinetics in this fundamental oxidation reaction of oxygen, Fe(II), and tartaric acid under wine-like concentrations across multiple pH levels. The stoichiometric response from the dissolved oxygen and Fe(III) time traces, combined with hydrogen peroxide time traces, have allowed for a more complex mathematical description than previously proposed for wine oxidation chemistry. The autocatalytic features, lag, propagation, and termination, are discussed with their dependence to pH. Additionally, lag, propagation, and termination were modified by adding varying wine constituents (malic, succinic, ethanol) and intermediates (hydrogen peroxide).

Materials and Methods

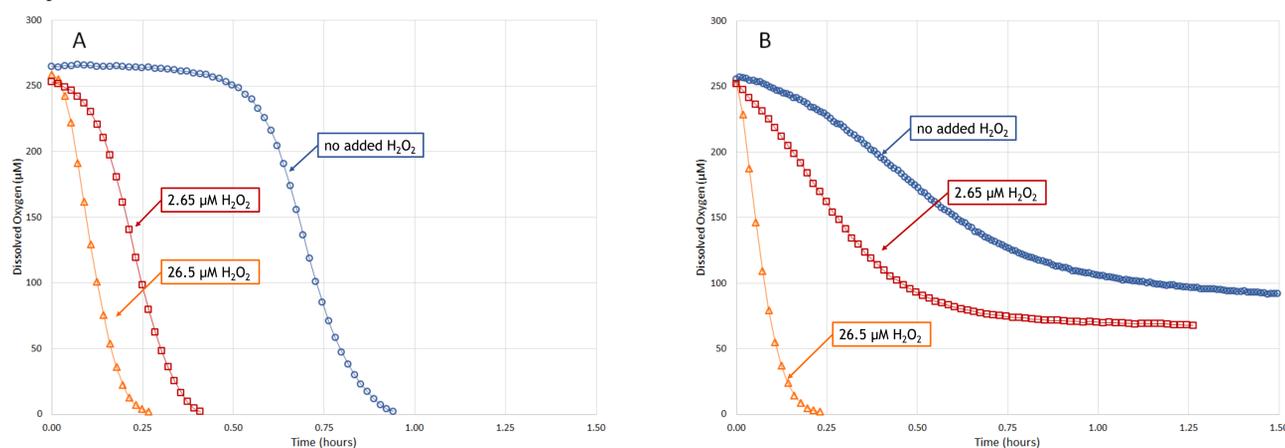
An OxySense@310 oxygen analyzer was used with an OxyDot (O2xyDot®) sensor affixed to the bottom of a Kimble Chase flat bottom 10 mm NMR tube to measure dissolved oxygen. Direct spectrophotometric Fe(III) measurements were taken by an UV-VIS Agilent Cary 60 spectrophotometer fitted with a C Technologies 10 mm path length quartz dip probe. A modified decolorization assay was developed to allow for quantification of hydrogen peroxide in low pH tartaric acid/Fe(II) solutions.¹ Spectrophotometric measurements for the decolorization assay were carried out using a ThermoFisher Genesys 10S UV-Vis spectrophotometer with 10 mm path length Starna quartz cells.

Kinetic measurements were carried out in a blackened 250 mL round bottomed flask with a PTFE magnetic stir bar. The temperature was held constant in a 20 °C water bath. The flask was fitted with rubber septa which housed the 10 mm NMR tube with affixed OxyDot and the 10 mm path length quartz dip probe. Headspace atmosphere was expelled when the probes were added, and the septa prevent atmospheric ingress of gases. To initiate the oxidation reaction, 1 mL of air-saturated tartaric acid was removed from the flask, and subsequently replaced by 1 mL of concentrated Fe(II) sulfate. The trialed Fe(II) concentration for this work was 265 μM (approximately the molar equivalent of oxygen in an air-saturated solution). The tartaric, malic, and succinic acid starting concentration was 26.7 mM (or 4 g/L tartaric acid). The solution was air-saturated prior to initiation of the reaction with Fe(II).

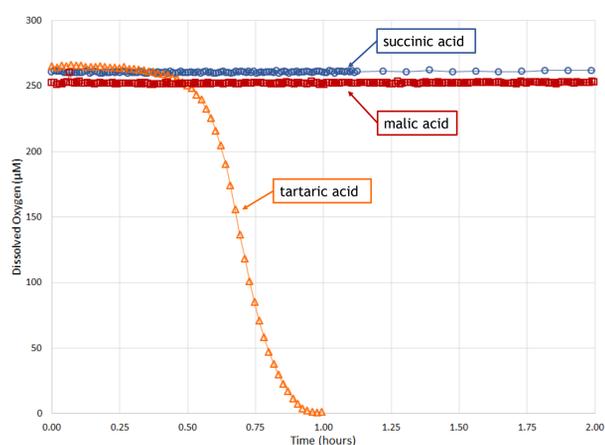
Results



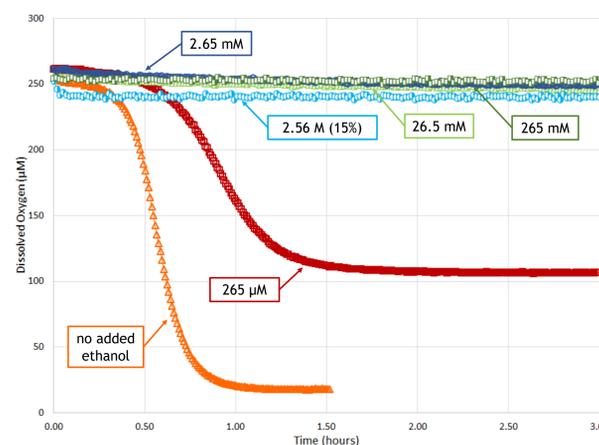
▲ **Figure 1** Dissolved oxygen consumption (A), Fe(III) formation (B), and hydrogen peroxide (C) time traces across pH levels. Both the dissolved oxygen and Fe(III) time traces show sigmoidal-like curves with distinct autocatalytic phases: lag, propagation, and termination. The propagation rate differs from general autocatalytic kinetics in that the rate appears constant and zero order with respect to both dissolved oxygen and Fe(III). Hydrogen peroxide acts as a true chemical intermediate in that it is formed and consumed in the reaction. Dissolved oxygen, Fe(III), and hydrogen peroxide time traces are pH dependent, as well as Fe(II)-tartrate complex dependent.



◀ **Figure 2** The addition of known concentrations of hydrogen peroxide at initiation for pH 2.5 (A) and pH 4.5 (B). At 26.5 μM initial hydrogen peroxide, the dissolved oxygen time traces are nearly identical, which indicates formation of hydrogen peroxide during lag or initiation phase.



◀ **Figure 3** Dissolved oxygen time traces of tartaric, malic, and succinic acid at pH 2.5. The autocatalytic nature of tartaric acid differentiates from the other major dicarboxylic organic wine acids. At pH 2.5, malic and succinic acid fail to significantly consume dissolved oxygen over the test time course. At pH 4.5 (data not shown), malic acid shows a slow linear decline of dissolved oxygen, while succinic appears to be unreactive.



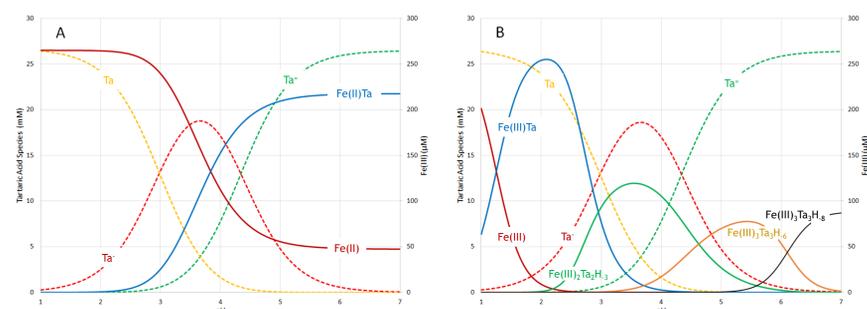
◀ **Figure 4** Dissolved oxygen time traces with various concentrations of added ethanol at pH 3.5. Over the tested pH levels, 2.5, 3.5, and 4.5, small concentrations of added ethanol (2.65 mM) significantly inhibited the autocatalytic nature of this reaction. At pH 4.5 (data not shown), 15% ethanol exhibited a slow, but steady decline in oxygen consumption as compared to pH 2.5 and 3.5.

Conclusion

Tartaric acid in the presence of Fe(II) and dissolved oxygen reacts in an autocatalytic nature with respect to Fe(III) formation and dissolved oxygen consumption. This autocatalytic nature is unique to tartaric acid, and not to the other significant dicarboxylic organic acids found in wine. As noted from the time traces, this reaction generates measured hydrogen peroxide as predicted by previous authors. The maximum accumulation of hydrogen peroxide corresponds closely to the complete consumption of dissolved oxygen, not at the midpoint of propagation. Each of the measured time traces, dissolved oxygen, Fe(III), and hydrogen peroxide, shows pH dependence. This pH dependence indicates the significance of Fe(II)-tartrate complexes in the observed oxidation kinetics. This Fe(II)-tartrate species dependent activation of oxygen is independent of ethanol and wine phenols

The addition of exogenous hydrogen peroxide at initiation indicates the formation of hydrogen peroxide during lag phase. The results indicate that if given enough hydrogen peroxide during initiation, the resulting propagation becomes pH independent.

Lastly, small quantities of ethanol (2.65 mM) were shown inhibit the autocatalytic nature of this reaction. Though dissolved oxygen consumption time traces did not show the sigmoidal-like shape in the presence of 15% ethanol, the higher pH levels tested showed significantly more oxygen consumption than at low pH levels.



▲ **Figure 5** Fe(II)-tartrate² (A) and Fe(III)-tartrate³ (B) speciation.

References:

1. Coleman, R. (2019). *Kinetics of Oxygen Consumption in Solutions of Iron and Tartaric Acid*. (PhD). University of California, Davis.
2. Timberlake, C. F. (1964). Iron-tartrate complexes. *J. Chem. Soc.*, 1229-1240.
3. Yokoi, H., Mitani, T., Mori, Y., & Kawata, S. (1994). Complex formation between iron(III) and tartaric and citric acids in a wide pH range 1 to 13 as studied by magnetic susceptibility measurements. *Chemistry Letters*, 23(2), 281-284.