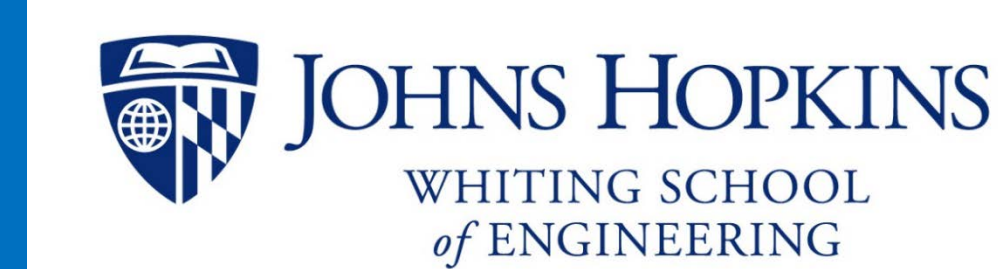


Permanganate Oxidation of α -Hydroxycarboxylic Acids: Hammett Relationship and Metal Ions Catalysis

Xiaomeng Xia and Alan Stone
Department of Geography and Environmental Engineering
Johns Hopkins University

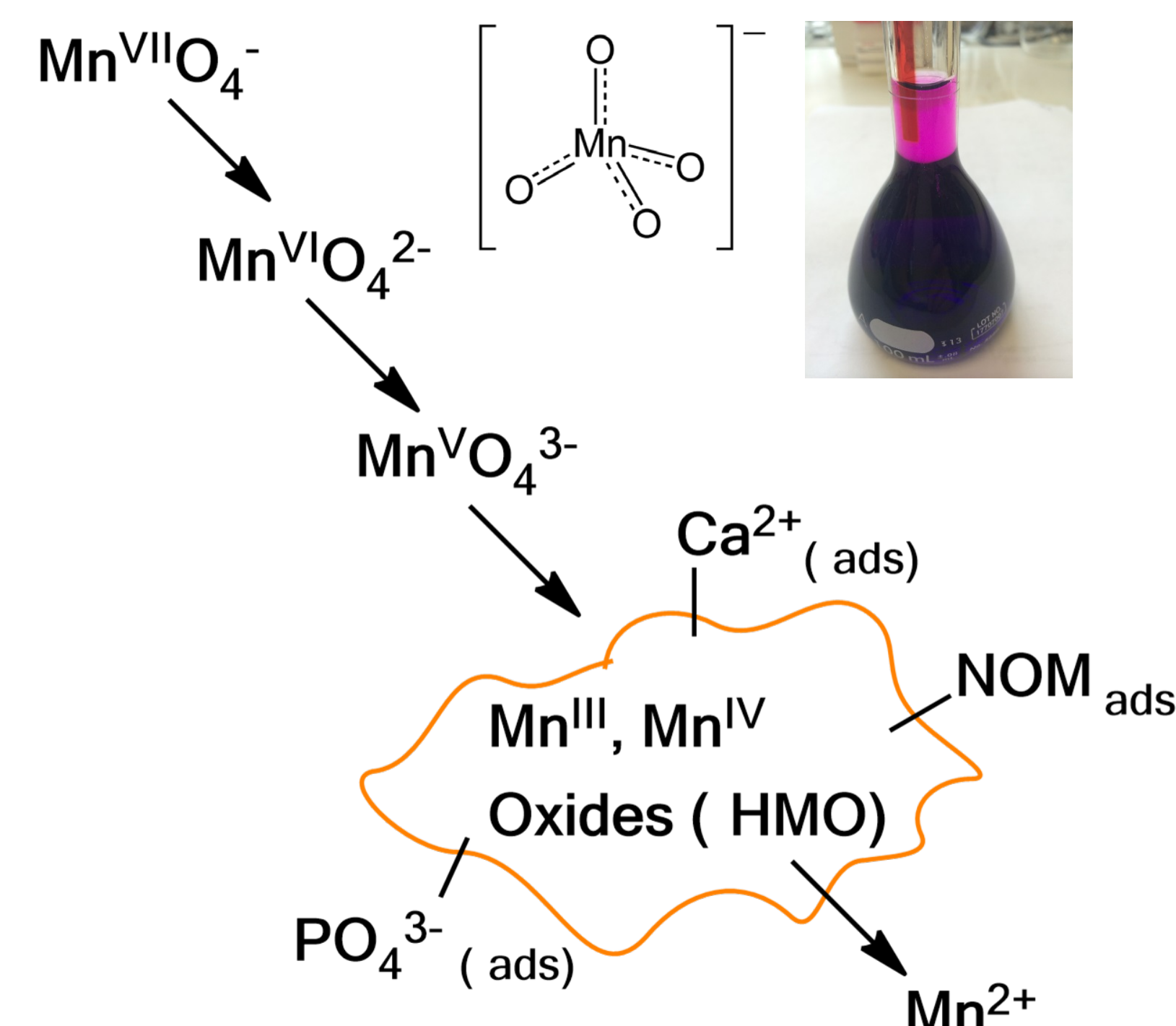


Introduction

Permanganate

Permanganate is widely employed in water supply plants before rapid sand filtration in order to:

- oxidize Fe^{2+} and Mn^{2+} ;
- control taste and odor compounds;
- remove organic toxins.



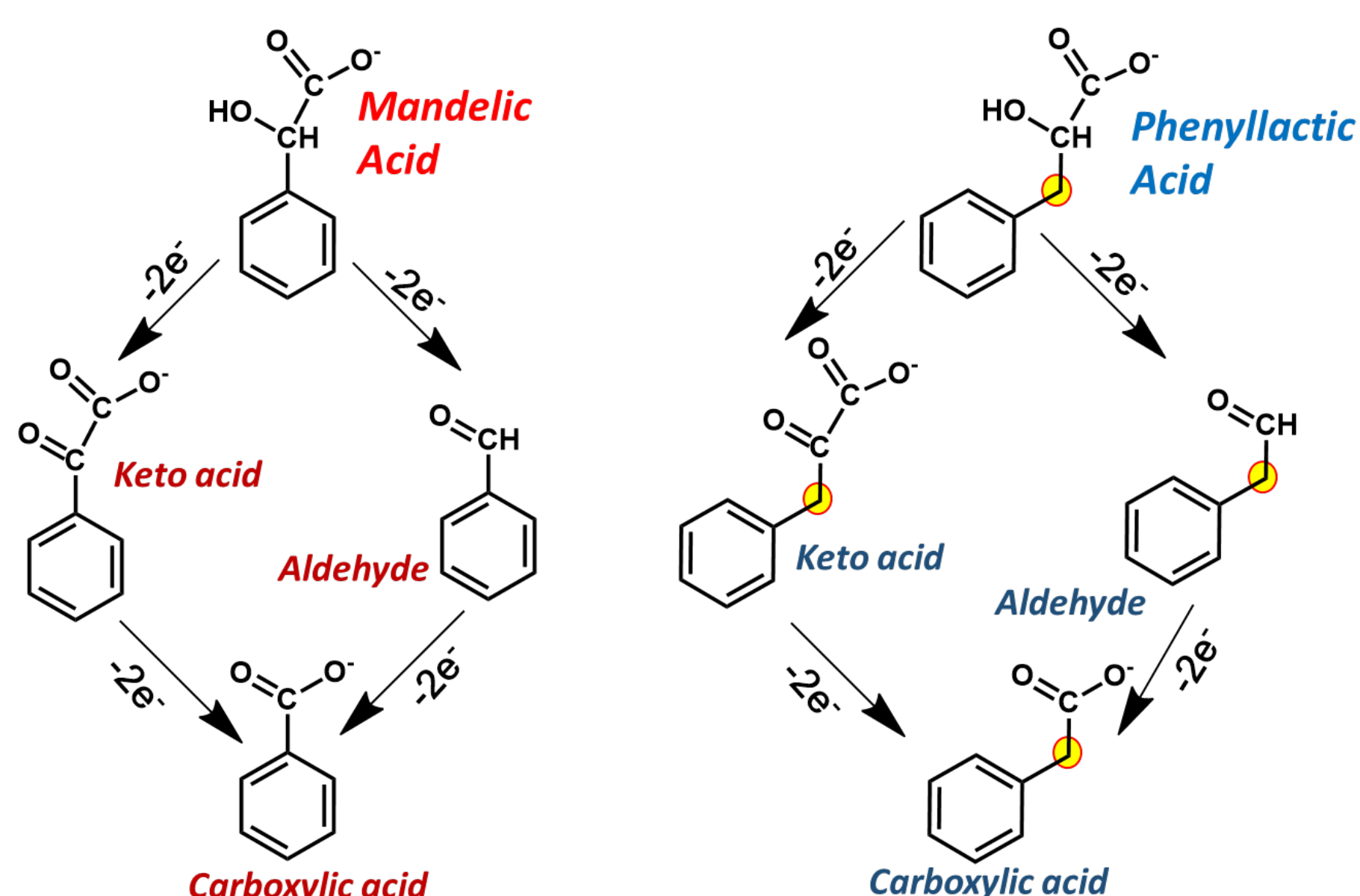
Permanganate oxidation is a multi-step reaction. Manganese oxidation state is reduced from +7 to +2. Hydrated manganese oxides (HMO) is the major intermediate which can serve as a second oxidant.

α -Hydroxycarboxylic Acids

α -Hydroxycarboxylic acids exist in both natural organic matter and lots of pharmaceutical and cosmetic products.



Oxidation of α -hydroxycarboxylic acids includes three intermediates and products. Phenyllactic acid possesses an extra $-\text{CH}_2-$ group which greatly affects reactivity and product identity.



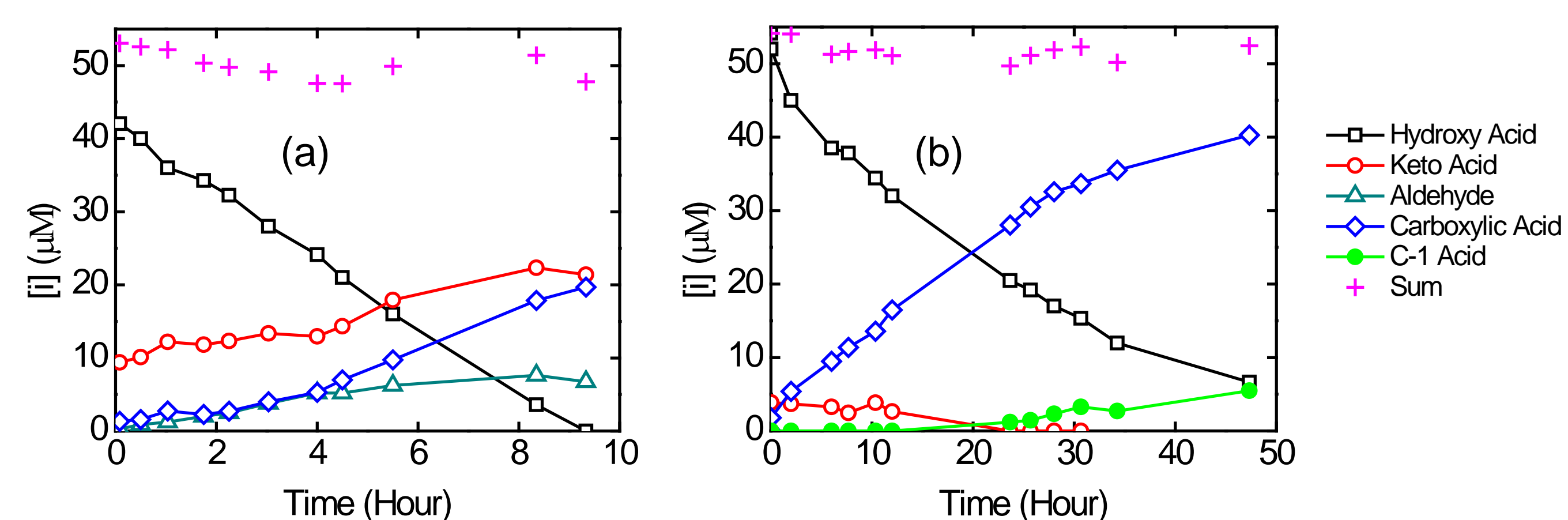
Objectives

The objectives of this study are

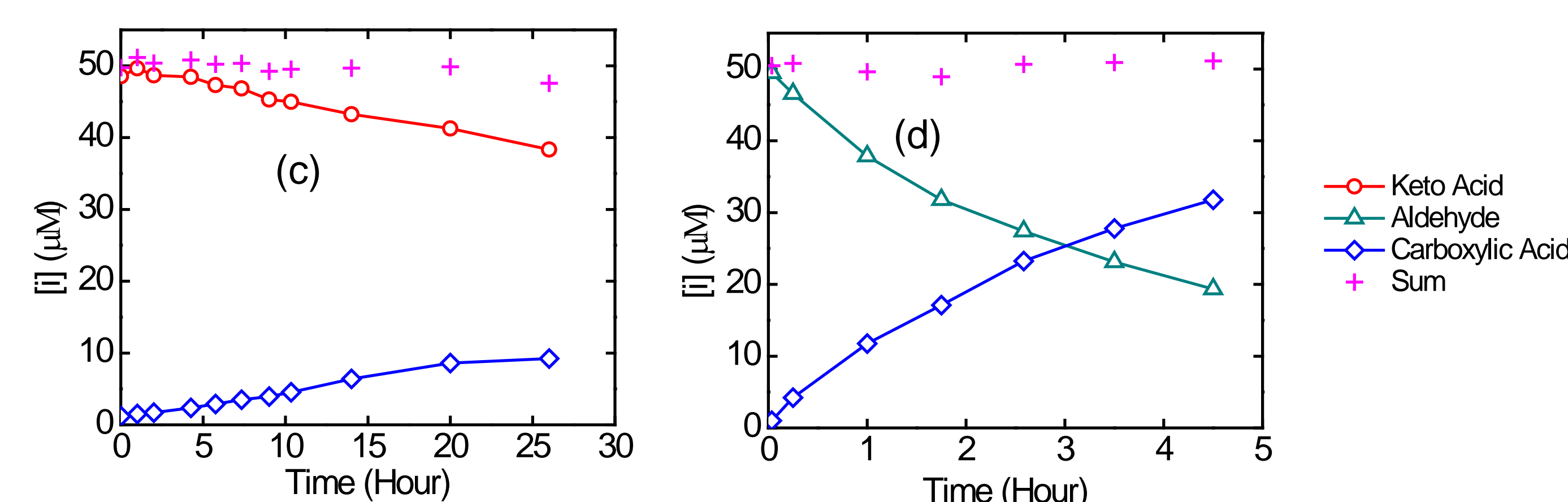
- to understand the kinetics and mechanisms of α -hydroxycarboxylic acids oxidation by permanganate.
- to develop the basis for predicting rates and products from structure.
- to assess the catalytic effects of metals.

Reaction Kinetics and Products

Permanganate

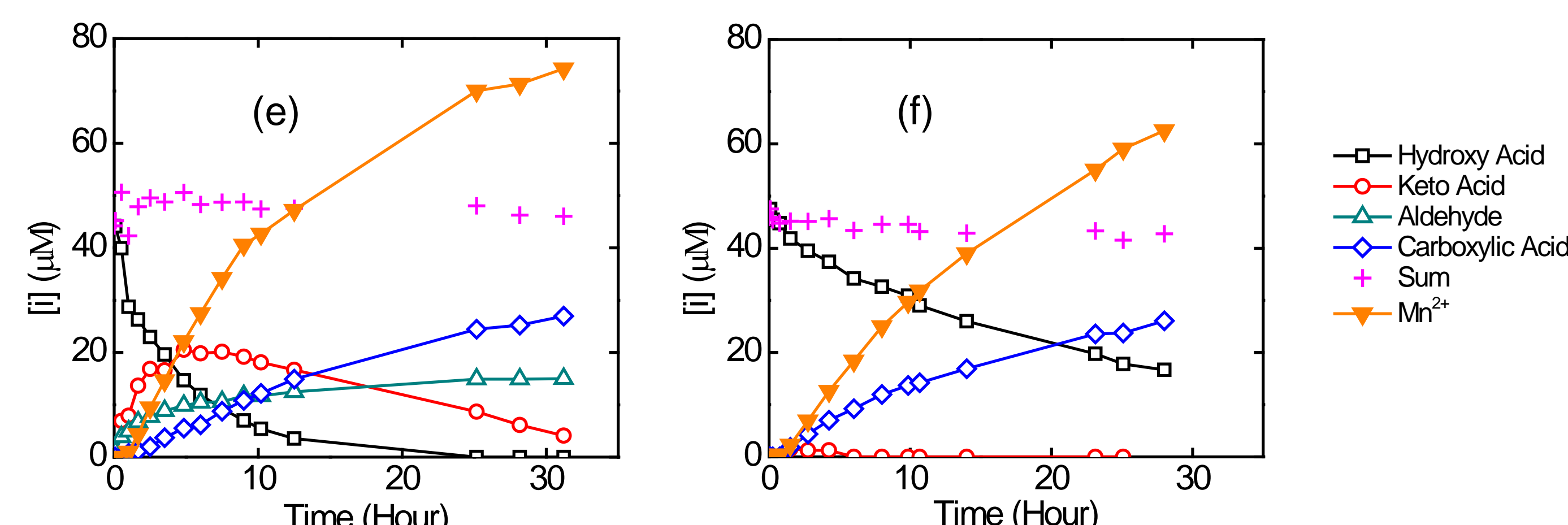


Reactions between 50 μM α -hydroxycarboxylic acid and 200 μM MnO_4^- in 5 mM acetate buffer (pH 4.0) and 10 mM NaCl. Same buffer and electrolyte was applied in all reactions unless otherwise noted. (a) mandelic acid and (b) phenyllactic acid.



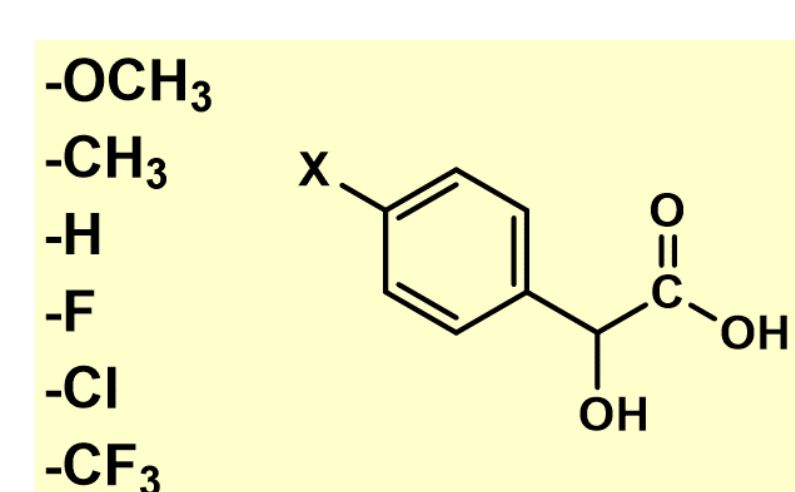
Reactions between 50 μM oxidation intermediates of mandelic acid and 100 μM MnO_4^- . (c) keto acid and (d) aldehyde.

HMO



Reactions between 50 μM α -hydroxycarboxylic acid and 500 μM HMO. (e) mandelic acid and (f) phenyllactic acid.

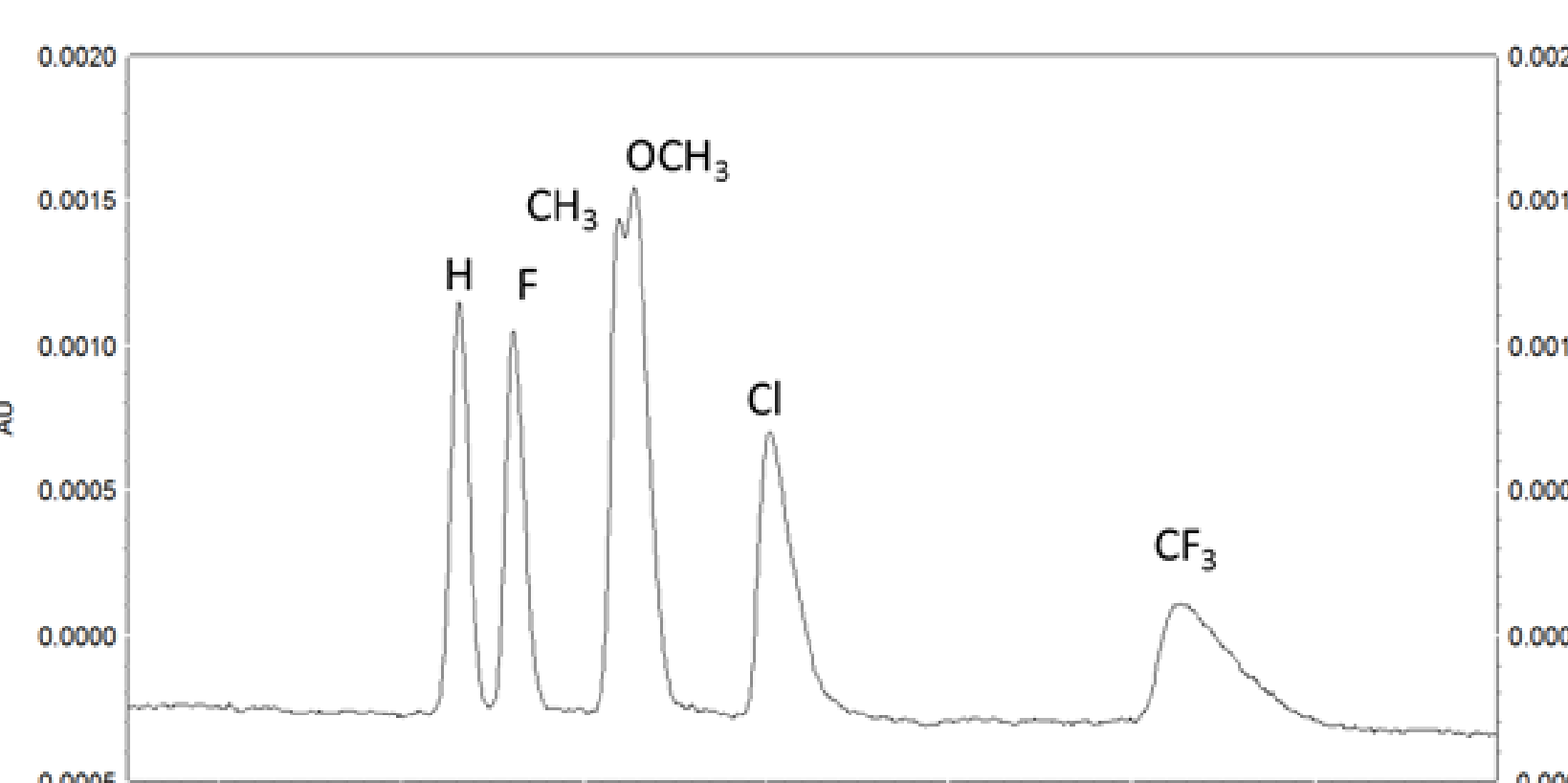
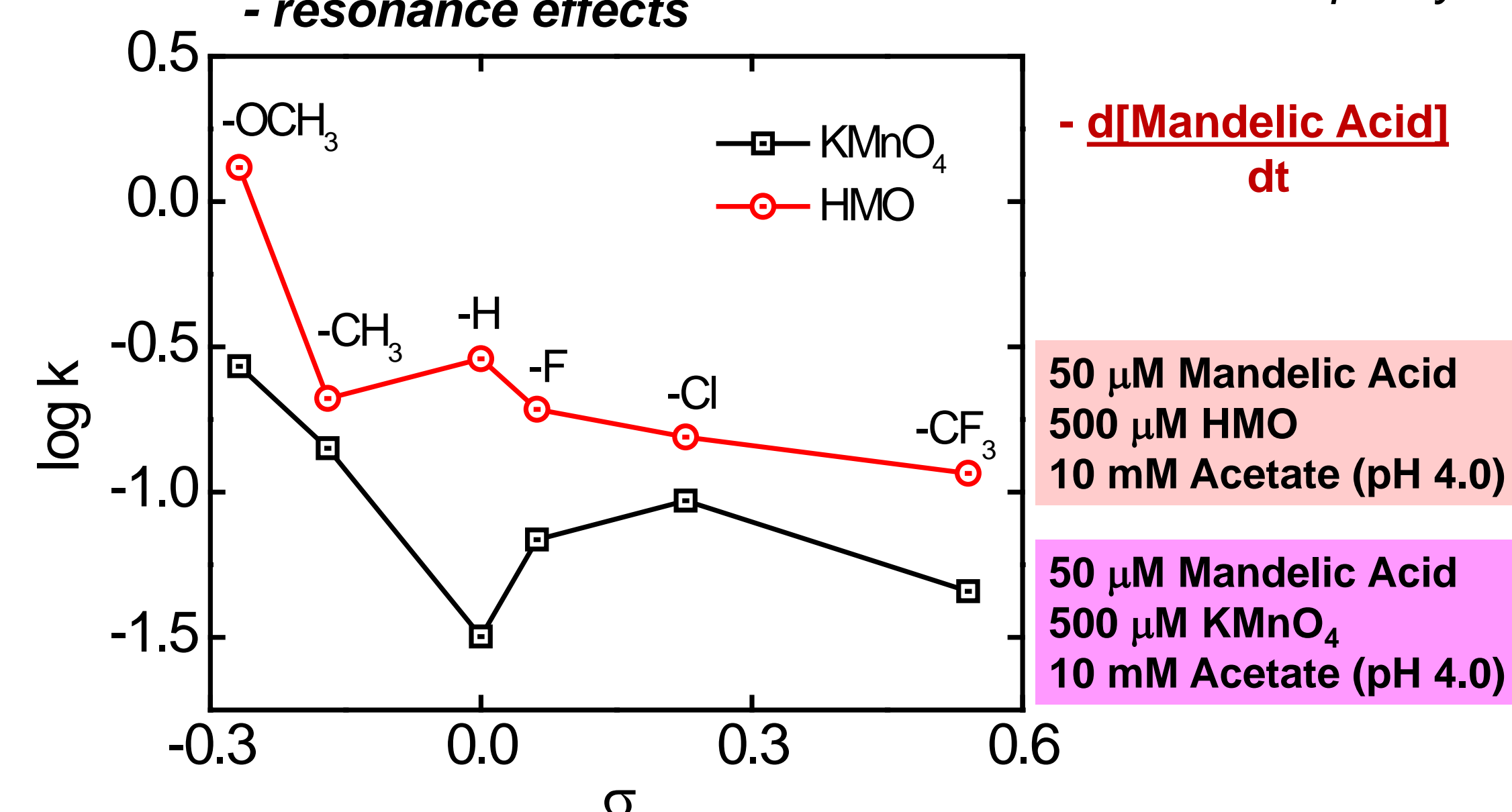
Substituent Effects – Hammett Like?



$$\log \left(\frac{k}{k_0} \right) = \rho \sigma$$

Hammett Equation only addresses electronic effects!

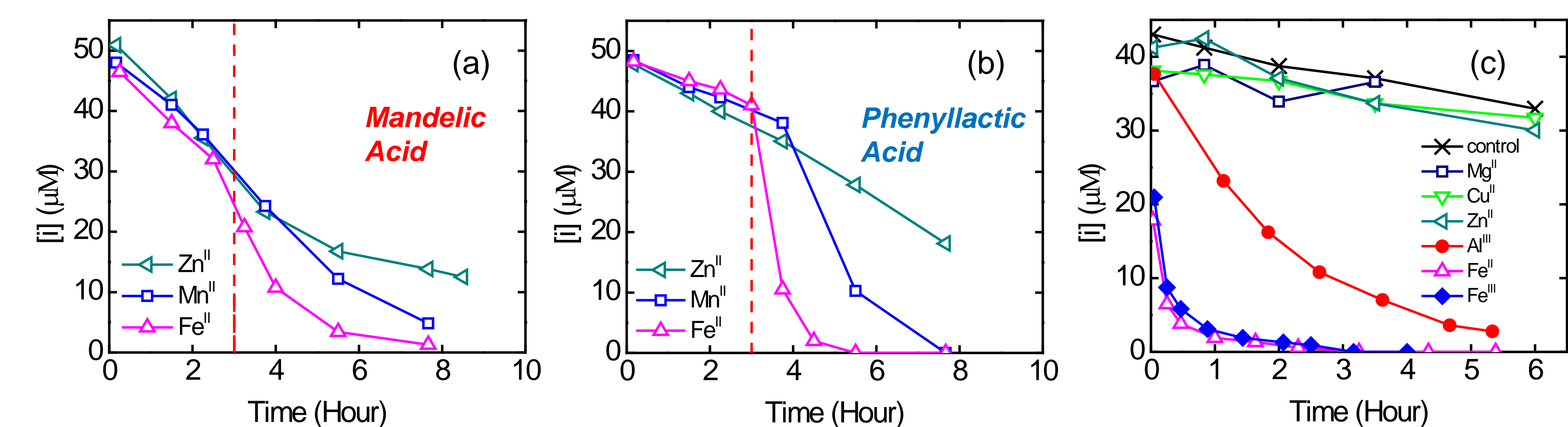
- inductive effects
- resonance effects



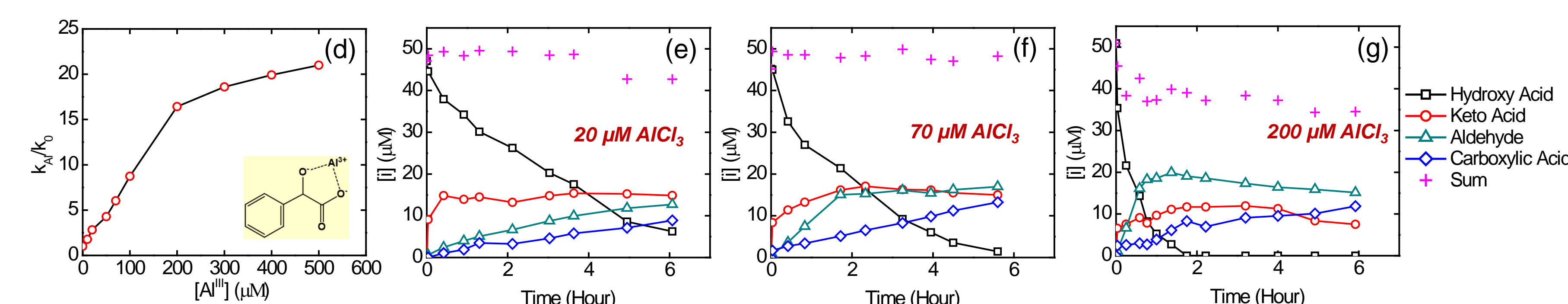
Electropherogram of six para-substituted mandelic acids under capillary electrophoresis anion mode.

Hammett Plots are not linear because (1) the substituents alter extents of adsorption on HMO and (2) two or more steps may be rate-limiting.

Metal Ions Catalysis

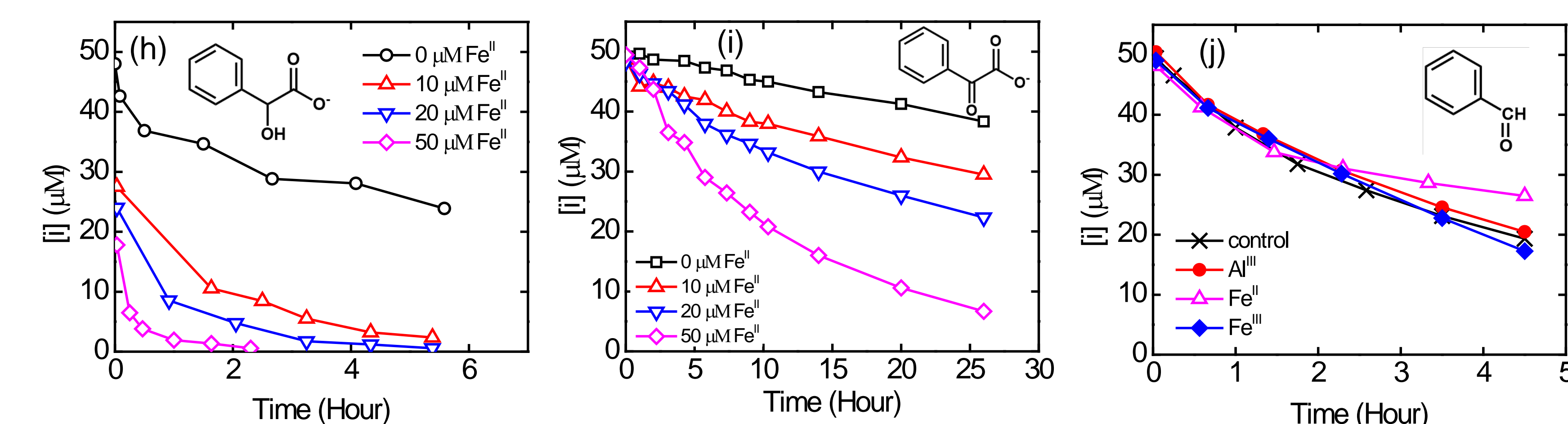


Reactions between 50 μM α -hydroxycarboxylic acid and 100 μM MnO_4^- : (a) Mandelic acid and (b) Phenyllactic acid with 10 μM metal chloride added at 3 hours of reaction. (c) Mandelic acid with 50 μM metal chloride added at the beginning of reaction.



Reactions between 50 μM mandelic acid and 100 μM MnO_4^- with increasing addition of AlCl_3 . (d) Saturation kinetics of Al^{3+} catalysis. Al^{3+} coordination with organic substrate.

Ratio of organic products changes with increasing Al^{3+} concentration. (e) 20 μM AlCl_3 , (f) 70 μM AlCl_3 , (g) 200 μM AlCl_3 .



Reactions between 50 μM (h) mandelic acid, (i) keto acid and 100 μM MnO_4^- with increasing addition of FeCl_2 .

(j) Reactions between 50 μM benzaldehyde and 100 μM MnO_4^- with addition of 50 μM metal chloride. No catalytic effect observed because there is no spot for metal coordination.

Concluding Remarks

- Phenyllactic acid with an additional $-\text{CH}_2-$ group is much less reactive than mandelic acid. In addition, the keto acid and aldehyde products are not seen. The additional $-\text{CH}_2-$ group increases extents of hydration and keto-enol tautomerization, shortening lifetimes of these products.
- Substituent effects although complicated, provide valuable insight into mechanisms.
- As expected, the redox active metals Mn^{II} , Fe^{II} , and Fe^{III} catalyze permanganate reactions. To our surprise, dissolved, redox inert Al^{III} coordinates hydroxycarboxylates and activates them towards reaction with permanganate.

Acknowledgements

The authors acknowledge the support from the National Science Foundation under Grant NSF CBET-1067075.

