



## Autocatalytic Profiles of Mn<sup>II</sup> Oxidation by O<sub>2</sub> for Different Ligands and pH Conditions

The oxidation of Mn<sup>II</sup> by oxygen, as tracked by the concentration of [OxMn] produced vs. time, is shown in Figures S1–S3 for the different experimental conditions utilized. At pH 10.19, the highest pH condition examined, oxidation of 50 μM Mn<sup>II</sup> plateaus at [OxMn]<sub>max</sub> = 72.2 μeq/L after *ca.* 40 min when no multidentate ligands are present in solution (Figure S1). Assuming all of the initial Mn<sup>II</sup> has been oxidized at this point, the solid product has an average oxidation state of manganese (Mn-AOS) equal to 3.44 and a stoichiometric formula equivalent to MnO<sub>1.72</sub>. As shown in all three panels of Figure S1, with increasing concentration of the different multidentate ligands tested, from zero up to the initial stoichiometric ratio [L]<sub>T</sub>/[Mn<sup>II</sup>]<sub>T</sub> = 1, the rate of Mn<sup>II</sup> oxidation slows down appreciably: the oxidation profile curves shift to the right and down with increasing dose of ligand. A qualitative comparison of the different panels in Figure S1 reveals that all ligands slow down Mn<sup>II</sup> oxidation at pH 10.19, albeit to varying extents. For example, as the initial stoichiometric ratio of [L]<sub>T</sub>/[Mn<sup>II</sup>]<sub>T</sub> approaches 1, EDTA, tripolyphosphate and pyrophosphate nearly completely shut down Mn<sup>II</sup> oxidation by O<sub>2</sub>. In contrast, 50 μM oxalate only slows down the oxidation rate by about half.

Figure S2 shows the effects of pyrophosphate (left) and EDTA (right) on Mn<sup>II</sup> oxidation at pH 9.65 for different initial Mn<sup>II</sup> concentrations. Consistent with Figure S1, increasing amounts of added ligand shift the profile curves to the right and down for both pyrophosphate and EDTA. Note that the experiments at pH 9.65 were stopped well short of reaching their expected plateaus, which would have been [OxMn]<sub>max</sub> ≈ 133, 67 and 33 μeq/L for the initial Mn<sup>II</sup> concentrations of 200, 100 and 50 μM, respectively. Fewer experiments were conducted at pH 9.42 (Figure S3) due to the slower oxidation kinetics with decreasing pH. Once again, however, it can be seen that oxalate is not as effective as pyrophosphate at slowing down the Mn<sup>II</sup> oxidation rate when the initial ligand to manganese ratio is one.

## List of Figures

- Figure S1. Profiles of Mn<sup>II</sup> oxidation by O<sub>2</sub> in the absence and presence of strong complexing ligands at pH 10.19. All solutions had an initial concentration of 50 μM Mn<sup>II</sup>(aq) and initial ligand concentrations are shown by their respective curves.
- Figure S2. Profiles of Mn<sup>II</sup> oxidation by O<sub>2</sub> in the absence and presence of strong complexing ligands at pH 9.65. Solutions had an initial concentration of 50, 100 or 200 μM Mn<sup>II</sup>(aq) as indicated in each panel and initial ligand concentrations are shown by their respective curves.
- Figure S3. Profiles of Mn<sup>II</sup> oxidation by O<sub>2</sub> in the absence and presence of strong complexing ligands at pH 9.42. All solutions had an initial concentration of 200 μM Mn<sup>II</sup>(aq) and initial ligand concentrations are shown by their respective curves.







## Odyssey through manganese, O<sub>2</sub>, and ligands

Composed by Jim Morgan, 2013

### Prologue.

In October 1967 Halka Bilinski joined my lab as a post doc from Zagreb. I asked her to study the effect of various ligands on the course of O<sub>2</sub> oxidation of Mn(II) in solutions. Her first experiments were designed to find the solubility of Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>(s) and the stability of Mn<sup>2+</sup>/P<sub>2</sub>O<sub>7</sub><sup>4-</sup> species in water. In the second phase of her research she followed the course of the Mn(II) oxidation in carbonic buffers, in absence or presence of “strong” ligands, e.g., EDTA. She measured the equivalent sum\*\* [OxMn] = [Mn(III)] + 2[Mn(IV)] vs time (on a scale of ~ 2 hr). Halka reported her results at the ACS Meeting in April 1969. A required “Extended Abstract, NOT FOR PUBLICATION,” 7 pages long, summarized both parts of her Caltech research. That was at a time before the creation of REDEQL. We were able to compute Mn<sup>2+</sup> and MnOH<sup>+</sup> initial concentrations by hand. The qualitative impression gained was that each of four ligands (P<sub>2</sub>O<sub>7</sub><sup>4-</sup>, EDTA, P<sub>3</sub>O<sub>10</sub><sup>5-</sup>, and oxalate slowed initial rate of oxidation, with some suggestion that P<sub>2</sub>O<sub>7</sub><sup>4-</sup> had a stronger effect on initial rates than the other ligands.

### Neka professorica to uciniti.

As time progressed, Dr. Bilinski chose not to pursue any further interpretations of her data. However, back in Zagreb, she later repeated the work on solubility and complexes. She published it in the journal *Polyhedron*, 1983.

### Divertimento.

Werner Stumm decided that an apparent difference in P<sub>2</sub>O<sub>7</sub><sup>4-</sup> influence on Mn(II) oxidation was noteworthy, and decided to copy a figure from our Extended Abstract. It appeared as Fig 6-16, p. 295, 1<sup>st</sup> edition of *Aquatic Chemistry*, 1970. I believe that is as close to being published as any of our 1969 data came.

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\*\* In 1965 Morgan and Smith reported the first use of leuco crystal violet dye to measure oxidizing equivalents of manganese oxides. In 1972, Vuceta, *et al* published a method for the measurement.

### Zwischenspielen.

A hypothesis that ligands forming Mn(II) complexes could *slow* oxidation by O<sub>2</sub> was incorporated in the second of two articles by Pankow and Morgan on metal oxidation in 1981. The parameters of autocatalytic oxidation were taken from Windsor Sung (1980), who fit the kinetic data from Morgan's 1964 thesis. Those "forward models" were not compared with data of Bilinski, for which no rate law had then been formulated. In 1980 Donald Wilson reported that oxalate and humic acid each slowed Mn(II) disappearance through reaction with O<sub>2</sub> at pH 9.0 in borate buffer. No rate law with ligands was proposed.

### Have we any X?

An assumption underlying the foregoing researches was that there was a product, "MnO<sub>x</sub>", whose properties were reflected in the heterogeneous rate constant,  $k_2$ . In 1974 postoc Mike Kessick conducted a Mn(II) + O<sub>2</sub> experiment in pH 9.0 ammonia buffer, identifying the oxidation product as MnO<sub>1.45</sub> (gravimetric analysis, time of reaction *ca.* 2 hr).

Speciation of Mn(III) and consequent differences in stability was the subject of Ken Klewicki's thesis research (1991-1995). He examined the kinetic stability of complexes of Mn<sup>3+</sup> with the ligands EDTA, P<sub>2</sub>O<sub>7</sub><sup>4-</sup>, and citrate. He found pH and ligand concentration effects on rates of Mn(III)-ligand species decomposition. In a related series of experiments, he found that MnOOH solid was dissolved by the same ligands at different rates, with both Mn(II) and Mn(III) species formed. In this work he observed that citrate in excess speeded the *re-oxidation* of Mn(II)-citrate to Mn(III). Ken's results were a motivation for me to take up again (after many years) the Mn(II) + L + O<sub>2</sub> story.

I first needed to interpret earlier observations on the lead term (the *homogeneous reaction term*) in an autocatalytic model of Mn(II) + O<sub>2</sub> rate, i.e.,  $-d[Mn(II)]/dt = k_1 [Mn(II)]$ . Rate constant  $k_1$  had been evaluated at lower pHs and with lower Mn(II) concentrations, under which conditions the catalysis term would be negligible. Absent "strong" ligands, how did  $k_1$  depend on pH and all Mn(II) species in solution? My paper in 2005 offered a partial answer. Carbonate, sulfate, chloride, ammonia, as well as hydroxide influenced the rate of solution oxidation. A speciation equilibrium model for Mn(II) was used to fit reported  $k_1$  values for seawater and laboratory



experiments. I emulated the approach used by King in 1998 to interpret Fe(II) oxidation data. I found a few reactive species responsible for the observed Mn(II)  $k_1$  values. Total carbonate could either speed up or slow down the oxidation rate. (More experimental data would have made the fit more robust; there were 15 results then for  $k_1$ .)

Around 2009, I started thinking that it might yet be possible to produce a quantitative explanation for the results of Bilinski (1969). A key could be improved speciation of Mn(II). There were 28 experiments to interpret: with three pHs, three Mn(II) concentrations, and the ligands EDTA, pyrophosphate, tripolyphosphate, and oxalate. I scrutinized our 1969 data and found a calibration error: [OxMn] values were too low by a factor of 2, thus making all observed initial rates too low by the same factor. Halka's kinetic data were available only as hand-drawn graphs of [OxMn] vs time. I digitized graphs (after correcting for the original calibration error).

My first effort at a fresh interpretation was to compute initial Mn(II) species ( $t = 0$  conditions). Plots of  $(d[\text{OxMn}]/dt)_0$  against  $[\text{Mn(II)Ligand}]_0$  were found to be systematic, i.e., with increasing [Mn(II)-Ligand] a steady decrease in initial oxidation rate occurred for both EDTA and pyrophosphate ligands. (Only a few initial rate data for oxalate or tripolyphosphate were available.) As  $[\text{Ligand}]_T$  approached  $[\text{Mn(II)}]_T$ , the oxidation rate approached zero in many cases. Initial rates approximated those computed with reactive species rate constants in the 2005 paper. An encouraging observation, but extensive observations of [OxMn] vs time still required interpretation. One worrisome aspect of those experiments with  $[\text{Ligand}]_T = 0$ : initial rates seemed too high in comparison to the extrapolated values from experiments at  $\text{pH} < 9.2$  (2005). For that reason, I considered omitting the ligand-free experimental conditions in the kinetic analysis.

I elected to use the autocatalytic model of Mn(II) oxidation, as interpreted by Windsor Sung in 1980. Kinetic constants  $k_1$  and  $k_2$  of the model were to be found from the kinetic data, [OxMn] vs time. Experimental variables were pH,  $[\text{Mn(II)}]_T$ , and  $[\text{Ligand}]_T$ .

zum Schluss (by MAS).

In an interview with Dianne Newman published in 2015 (*Annu. Rev. Earth Planet. Sci.* 2015, 43, 1-27), Jim discussed his “re-motivation” for  $\text{Mn(II)} + \text{L} + \text{O}_2$ :

*Now I told you that I said I had a theme and I was trying to implement it. And one of the themes was speciation. And with a postdoc, Dr. Halka Bilinski from Yugoslavia, we had a series of experiments which combined the two themes. How fast can manganese be oxidized? This is a laboratory study. And what are the species in the solution that either encourage or discourage the oxidation? Now I have to confess that, to this day, I am still working on the final publication from that data. I think it was more difficult than I realized; that is, to bring kinetics and speciation under the same roof, and to have a successful paper. So I'm still working on it, and I think probably by this time next year, we'll be able to submit it, maybe to ES&T.*

Sadly, it took us longer . . .