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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Photochemical degradation of iron(III)-citrate/citric acid aerosol quantified with the combination of three complementary experimental techniques and a kinetic process model" *by* Jing Dou et al.

Anonymous Referee #1

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The manuscript seeks to explore the effect of high viscosity on photochemical processes using iron(III)-citrate (FeIII(Cit)) as a model light absorbing iron carboxylate complex. To investigate kinetic transport limitations, three complementary experimental approaches were used: (a) The mass loss of single, levitated particles was measured with an electrodynamic balance, (b) the oxidation state of deposited particles was measured with X-ray spectromicroscopy, and (c) HO2 radical production and release into the gas phase was observed in coated wall flow tube experiments. Also, a numerical multi-layered photochemical reaction and diffusion (PRAD) model that treats

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chemical reactions and transport of various species was developed.

Overall, the experimental and modeling approach is novel and the study is publishable after addressing the following major and minor comments:

Major comments:

Line 126-127: Figure 2 shows the data while irradiation, not while the particle is equilibrating. The data for this part of the experiment are shown over a much shorter time than the 10 h stated in the methods section. what is the magnitude of mass loss during the dark equilibration period?

There are conclusions made in the abstract that did not come across very clearly upon examining the figures and the text. It is important that each major statement on observations in the manuscript is supported by the data analysis in the manuscript. The figures need to be re-made to make conclusions easier to see for connection with the abstract. For example, the conclusion in line 17 was for 10 micron particles over 24 hr, but the modeling results in Figure 13 were for 1 micron to nanometer particles, and their mass loss rate is different. Also, data is Figure 6 show less than 80% mass loss.

In the abstract, the statement, “The PRAD model was tuned to reproduce all experimental results”: The mass loss data in Figure 2 does not show modeling results specific to the experimental setting to support this sentence. Also, model results in figures 7 and 11 are way off from the experimental data. So, it is not clear how this model reproduced the experimental data.

It is not clear how the molar ratio of Fe(III)(Cit) to citric acid (CA) was controlled. The manuscript shows that it was not fixed in the experiments, and the chemical composition was calculated. Section 2.1 does not describe solution preparation from which aqueous droplets were taken for the EDB measurements. The caption of the figures reported 0.01, 0.05, 0.07, and 1. How does these calculated molar ratios correlate with the solution prepared in the lab?

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What is the pH of the solution prepared in the lab and that calculated from the chemical composition model? What is the effect of pH on mass loss? Photochemical degradation of iron complexes is pH dependent, not only wavelength dependent. This is a major issue that is not addressed in the current version of the manuscript.

There was no experimental studies looking at the extent of mass loss as a function of molar ratio, as there was for particle radius and %RH (e.g., figure 13).

Figure 10: per the mechanism in Figure 1, and the abstract line 4,5 “In the presence of O2, ensuing radical chemistry leads to further decarboxylation, and the production of .OH, HO.2, peroxides, and oxygenated volatile organic compounds, contributing to particle mass loss”, I expected the opposite result for the ‘mass remaining’ data in the right axis: that the mass remaining for the particle recovered in O2 for 45 min is lower than irradiating fresh particle under N2 since the photolysis and loss of CO2 is driven by the chemistry of dissolved O2. I did not find an explanation in the text for this part of the figure.

Minor:

Line 418: The reference Duo et al 2020 is not published. The sentence citing this reference does not refer to unknow information. There are book chapters and numerous review articles on this topic, which should be cited.

Figure 2: for consistency with the text, change the y-axis to hours instead of seconds for time since rates and time discussed in the text are expressed in hours.

Figure 3: there are two shaded areas in dark and light green, and only the light green is described in the legend. There seems to be a missing compound that describes the dark green shaded area. Also, it is not clear why there are references in the caption? Were some of the spectra shown adapted from these references?

Figure 6: the color description for RH does not match the actual colors of the markers. For example: in the figure, data for RH=33% is red, and in the caption is it mentioned

as ‘(black)’. In be, there are markers and lines, for experimental data and model results. Modify the legend to reflect that to avoid confusion which is which.

Figure 11: use different marker shapes for different RH, chemicals. Take into account that this figure might be printed on a black and white printer and will be hard to read as is. Why is here more than one data point at t $\sim$ 3 min for the RH = 48%? Same at t $\sim$ 15 min and 20 min for 48% and 65% for iron(II) and iron (III) citrate?

Figure 12: add a legend defining the markers and lines

Figure 13: add ‘RH=40%’ to legend in (a), and ’100 nm’ to legend in (b).

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