

Interactive comment on “Effects of temperature on the heterogeneous oxidation of sulfur dioxide by ozone on calcium carbonate” by L. Y. Wu et al.

Anonymous Referee #2

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This manuscript presents DRIFTS data investigating the heterogeneous reaction of sulfur dioxide and ozone on calcite surfaces. Although this system has previously been discussed in the literature, the current manuscript considers temperature effects between 230 and 298 K. The most notable claim is a “turning point” in the temperature effect around 250 K, which the authors attempt to explain in terms of competing factors between the “rate limiting step” for ozonolysis of surface sulfite versus the adsorption equilibrium for gaseous sulfur dioxide. This discussion of this temperature effect turning point, however, is presently not convincing. This and other major issues are numerated below:

1. Figure 1. Ordering of spectra is confusing. It seems as if the authors have ordered them by increasing sulfate intensity rather than temperature. If they believe this

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to be preferable, please clearly state this decision in the text and figure caption. Peaks around 875 cm⁻¹, which randomly seem to be positive and negative for different experiments, are not discussed in text. Presumably this is a contaminant – do the authors know their origin?

2. Figure 2. There appears to be absorption bands around 1790 cm⁻¹ (and possibly around 1650 cm⁻¹) underneath the poor water vapor subtraction. Again, the presence of organic contaminants might impact the experimental results – the authors should identify and discuss these bands in the text.

3. Labeling of the various kinetic regions is confusing. Given the low RH of these experiments, the decreasing rate of reaction likely results from surface sulfate blocking adsorption sites for further sulfur dioxide reactions. “Transition state” and “steady state” labels have other common meanings. Perhaps “transition region” and “saturation” would be less confusing descriptors.

4. The authors state that reaction 2 is rate determining. While this seems reasonable given their proposed mechanism, they present no evidence supporting this conclusion. Did they run any duplicate experiments with different ozone concentrations? All conclusions must be supported by observations.

5. Figures 5 & 7. As the authors state, “it is scarce that turning point appears at the experimental temperatures.” Unexpected results require conclusive supporting evidence. The experimental and data discussion, however, is lacking many details which the authors need to address to support the robustness of this data. How were the error bars determined? Were they the result of replicate experiments at each temperature? The “relationship between formation rate of sulfate and temperature” (i.e., Figure 5) matches that pattern of the t=200 minute concentration of sulfate vs. temperature (Figure 7). I am concerned that the effect of temperature on rate may simply be a result of the effect of temperature on the final sulfate IR signal – is this trend supported by replicate experiments? I do not understand the authors’ arguments for this trend. The

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authors should analyze each reacted sample using ion chromatography to confirm the linear correlation between their final sulfate IR signal (which was recorded at different temperatures) and the final analyzed IC sulfate concentration? Finally, what are the solid lines included in these figures?

6. Figure 6 is redundant since it simply shows three data points from Figure 5.

7. A rigorous discussion of the turning point is lacking from this paper. At present, they simply discuss why one might expect the rate to increase with temperature and why one might expect the rate to decrease with temperature. They fail, however, to explain their major claim which is how their system transitions from one relationship to the next. The arguments put forth by the authors should be consistent with the steady state equation (1) considering the temperature dependence of k_1 , k_{-1} , and k_2 – and I am not sure this is the case. This article requires extensive work and revisions that must include a convincing discussion and explanation of this observation.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 3493, 2011.

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