

## ***Interactive comment on “Mechanistic study of secondary organic aerosol components formed from nucleophilic addition reactions of methacrylic acid epoxide” by A. W. Birdsall et al.***

**Anonymous Referee #1**

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In this manuscript, the authors present an experimental study of the chemical mechanisms involving a newly discovered atmospheric epoxide: methacrylic acid epoxide (MAE). NMR spectroscopy is used to determine the kinetics, mechanism and relative nucleophilicity of different atmospheric compounds reacting with MAE in the liquid phase. The work is significant and timely considering that MAE was recently detected in the atmosphere and is derived from isoprene – a major contributor to global secondary organic aerosol (SOA). The manuscript is well written and addresses the need to improve atmospheric models that are currently being used to understand issues impacting air quality and climate change. I recommend this paper for publication in ACP

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after the following points have been addressed.

### General Comments

1. The abstract contains the following statement that is misleading and should be corrected: ‘However, the specific chemical mechanisms by which MAE could form these compounds have not been previously studied.’ The included citation by Piletic et al. (PCCP, 2013) has already reported on the stereochemistry and regioselectivity of the hydrolysis and oligomerization of atmospheric epoxides including MAE via computational methods. It is important to distinguish this work from the reference by emphasizing that this is an experimental study.

2. The authors measured the hydrolysis kinetics of MAE in D<sub>2</sub>SO<sub>4</sub>/D<sub>2</sub>O solutions (Section 2.3, pg. 19924) although they never discussed a kinetic isotope effect when comparing their results with other studies or real atmospheric aerosol. How might using D<sub>2</sub>O (instead of H<sub>2</sub>O which is present in the atmosphere) affect the hydrolysis rate constants? A discussion with a reference would be helpful to atmospheric modelers considering implementing these results in models.

3. Some of the statements in Section 3.2 are not accurate. On pg. 19926 (line 19), the authors mention that the rate-determining step of acid-catalyzed epoxide hydrolysis ‘is the protonation step’. The acid catalyzed hydrolysis of epoxides consists of the following steps:

- a) Protonation of epoxide
- b) Ring Opening
- c) Nucleophile bonding
- d) Deprotonation

Steps b) and c) are concerted in a purely A-2 (S<sub>N</sub>2) mechanism while separate in a purely A-1 (S<sub>N</sub>1) mechanism. The ring opening typically is the rate determining

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step while the protonation step will establish a pre-equilibrium during the reaction (see for instance Long F.A. et al. JACS, 1956, v. 78, p. 2663). Expansion of the rate law involving the protonated epoxide intermediate and the pre-equilibrium gives equation 1. Additionally, the statement at the bottom of pg. 19926 indicating that the concentration of the acid catalyst remains constant is not applicable in every reaction. In many cases, the attacking nucleophile (such as water, alcohol or carboxylic acid) will regenerate the acid. However, if the attacking nucleophile is an inorganic ion such as sulfate or nitrate, the acid is effectively consumed. This issue should be discussed in this section.

#### Specific Comments

1. What is a typical <sup>1</sup>H signal-to-noise ratio that is sufficient 'to allow for quantitative integration' (pg. 19923 line 23)?
2. The labels 'diether' and 'diester' in Figures 1, 2, 6, 7, 8 and 9 are not chemically correct even though they are defined by the authors on page 19932. The compounds as drawn do not possess two ether or ester functional groups as the label suggests. As mentioned on page 19932, they represent a dimer that is linked together by a single ether or ester linkage. This is confusing when looking at figures without reading the details in Section 3.4 of the text. I would recommend re-labeling as 'ether dimer' or 'ester dimer' or something similar.
3. Different acids were used (due to convenience and keeping chemical systems simple) to determine the relative nucleophile strengths (such as D<sub>2</sub>SO<sub>4</sub>, MAE, 2-MG). Does the nature of the acid affect the hydrolysis kinetics?

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