

Referee 1 (response in blue font)

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.

The qualifier, “with experimental methods,” has been added to this sentence.

2. The authors measured the hydrolysis kinetics of MAE in D₂SO₄/D₂O 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 D₂O (instead of H₂O 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.

We have added the following discussion of a potential kinetic isotope effect to Section 3.2:

“Due to possible kinetic isotope effects, the presently reported rate constant (measured in deuterated solvent conditions) may differ from the rate constant appropriate for aerosol environments (normal isotope solvent conditions). While this effect was not investigated in the present study, a previous acid-catalyzed epoxide kinetics investigation (Eddingsaas et al., 2010) estimated that deuterated solvent conditions lead to rate constants that are either equal to those for normal isotope solvent conditions (for S_N2-like mechanisms) or to rate constants as much as a factor of two larger than for normal isotope solvent conditions (for S_N1-like mechanisms).”

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_N2) mechanism while separate in a purely A-1 (S_N1) mechanism. The ring opening typically is the rate determining 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.

We have changed the relevant portion of Section 3.2 to address this issue:

“If the actual acid does not also act as a nucleophile, its concentration is constant over time, allowing for the substitution

$$k' = k[H^+] \quad (2)$$

where k' is the pseudo-first order rate constant. Sulfuric acid was used the acid source in these experiments. Although deprotonated forms of sulfuric acid can potentially compete with water in the nucleophilic addition process (and thus potentially decrease the acid concentration over time), the use of relatively low concentrations of sulfuric acid led to a situation in which the nucleophilic addition of water dominated for all conditions (as confirmed by the quantification of the nucleophilic addition products formed).”

Specific Comments

1. What is a typical ^1H signal-to-noise ratio that is sufficient ‘to allow for quantitative integration’ (pg. 19923 line 23)?

We have changed this sentence to more specifically address how this impacts the precision of the kinetics measurement:

“For these experiments, ^1H spectra were collected with 8 scans (30 s) which gave large enough signal-to-noise ratios to be able to follow MAE reactant loss over more than an order of magnitude of relative concentration.”

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.

We have added the following to Section 3.4 to rationalize and more specifically describe the nomenclature system:

“The nomenclature used to identify the various species in Figures 1,2,6 and 7 is intended to highlight the mechanistic route by which the species formed. For example, the *primary diester* name assigned to the species formed as shown at the bottom of Figure 7 reflects that this *dimeric*

species (formed from the reaction of MAE with 2-MG) is connected via a single *ester* linkage that formed at the *primary* epoxide carbon of MAE.”

3. Different acids were used (due to convenience and keeping chemical systems simple) to determine the relative nucleophile strengths (such as D₂SO₄, MAE, 2-MG). Does the nature of the acid affect the hydrolysis kinetics?

Formal hydrolysis kinetics were formed only with sulfuric acid. Therefore, we have no information concerning this potential effect.