

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 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.

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<sub>N</sub>2-like mechanisms) or to rate constants as much as a factor of two larger than for normal isotope solvent conditions (for S<sub>N</sub>1-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<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 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  $^1\text{H}$  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,  $^1\text{H}$  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 D<sub>2</sub>SO<sub>4</sub>, 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.

Referee 2 (response in blue font)

General Comments/Questions:

1) The authors mention in the introduction that the Fischer esterification of 2-MG could not account for observed oligomer formation in smog chamber experiments. How do the rate constant for hydrolysis of MAE presented here along with the measured relative nucleophilicities do in regards to predicting oligomer formation from MAE when compared to chamber experiments?

The MAE hydrolysis rate constant is about 30 times faster than the Fischer esterification rate constant, so this difference is significant (we have added this specific quantitative comparison to Section 4.1 of the revised manuscript). We also estimate in Section 4.1 that an effective pH of 0 is necessary for MAE reaction on the hour timescale (the timescale of the chamber experiments). While the relevant chamber experiments had no way to estimate effective acidity, an effective pH of 0 does not seem unreasonable (particularly for the lower RH experiments). By the same token, the relevant chamber experiments also had no way to estimate relative nucleophile concentrations, so it is not possible, using the relative nucleophilicities determined in the present study, to quantitatively predict the oligomer formation observed in those experiments.

2) How long were the prepared MAE and 2-MG stored prior to use? Was there any noticeable degradation over time? This seems like something that is important to mention because of, e.g., the presence of 2-MG in the self-reaction of MAE discussed in section 3.4.

Both MAE and 2-MG were stored at -80 C (this detail has been added to the manuscript for 2-MG) for as long as months before their use in the present experiments. The samples were observed to be very stable under these (frozen) conditions.

3) Can anything be said about the corresponding reaction to form nitrate esters based on your results and previous work exploring sulfate and nitrate ester formation from reactions of IEPOX (from, e.g., Eddingsaas et al. 2010)?

The following sentence has been added to Section 4.3 to address this issue:

“While the nitrate nucleophile was not directly studied in these experiments, because its relative nucleophilicity has been found to be similar to sulfate for reactions with isoprene-derived epoxides (Darer et al., 2011), it is expected that for MAE reactions that sulfate and nitrate would have similarly nucleophilicities. “

Specific comments/questions:

Page 19929, line 11. Is the second half of this sentence referring to the slow formation of 2-MG from MAE followed by reaction with sulfate, or is there some 2-MG present at the start of the reaction?

Even at 1 M sulfuric acid, the majority of MAE reacts to form 2-MG. Therefore, there is 2-MG being formed at the very beginning of the reaction, which could potentially react with sulfuric acid to form the sulfate ester. This sentence indicates that the observed kinetics rule out this two-step process.

Page 19930, Section 3.3.2. I would suggest including some figures of the spectra being discussed, perhaps as SI.

Because these spectra were collected in CD<sub>3</sub>OD solvent (as opposed to the D<sub>2</sub>O solvent used for the other experiments), the chemical shifts differ from the D<sub>2</sub>O solvent values given in Tables 1 and 2. While the CD<sub>3</sub>OD solvent spectra were used to establish bond connectivity information, the actual chemical shift values given in Table 1 and 2 were determined from Experiment #7, which was carried out in D<sub>2</sub>O solvent. Therefore, we feel that there is little benefit to including these spectra (and in fact, they may well be confusing since the chemical shift values are not directly comparable to the D<sub>2</sub>O values reported for all other species identified in this work).

Page 19930, lines 6. It's not immediately apparent what 'the 2-MG peaks' is referring to, and new peaks 'near' an existing peak could be more precise unless the spectra are shown.

We have added the actual chemical shift values to the text here so that it is clear how 2-MG and MAE-methanol species were distinguished.

Page 19931, line 14-18. Would the difficulty of forming a primary carbocation also suggest a more SN<sub>2</sub>-like mechanism?

Yes, this is the classic rationale for why SN<sub>2</sub> mechanisms can be favored over SN<sub>1</sub>.

Page 19932, lines 14-16. I think it would be helpful to include some quantification of the species present at the beginning of the reaction if possible. (See comment on Table 1) Given the slow hydrolysis of MAE and the conditions it is stored under, is this much 2-MG expected? (See general comment 2)

Page 19933, line 9. As per the previous comment, some estimate of the concentration of the water impurity may be useful.

Page 19943, Table 1. Although it is mentioned in the main text, I think there should be a comment in the table caption or as a footnote regarding how these values were calculated, because a mole fraction for MAE of 1.000 implies that no other species were present in concentrations  $> 5e-4$  mole fraction. However, as shown in Fig. 8 and discussed in section 3.4, there was a not-insignificant amount of water and 2-MG present at the beginning of experiment 4. Some indication of the important impurities present in each experiment should be made in the table. Also, an estimate of the error associated with the final measured concentrations should be included, if possible.

For the particular experiment of interest to the referee here, Experiment #4, we note that this experiment was only used for NMR and mechanistic interpretation purposes, and was not used in the calculation of the relative nucleophilicities. In particular, this specific MAE sample was an older, less pure sample than the MAE used in the other experiments. Indeed, the “fortuitious” water content of this sample allowed us to be able to observe all of the potential reactions of MAE with 2-MG that were eventually identified in the more controlled MAE/2-MG experiments (Experiments 5-7). In particular, it should be noted that the “early” reaction trace for Experiment #4 shown in Figure 8 is not from the very beginning of the reaction, but after a significant amount of time had elapsed. The “late” reaction trace is after much more time had elapsed. Therefore, the relatively large amount of 2-MG in the “early” trace is due to the reaction of MAE with water, not due to large impurities of 2-MG initially present in the MAE sample.

While we have no direct way to quantify the water impurity in this particular experiment, one can use the relative nucleophilicities determined from other experiments and the 2-MG to other product ratios to approximately back calculate the amount of water in this system. Based on this process, we estimate that water impurity was no more 0.2 mole fraction. We have edited Table 1 to reflect his estimate and have also included a note to specifically indicate that the uncertainty in the water content precluded the use of this experiment in the determination of the relative nucleophilicities.

We have added an estimate for the uncertainties in the product mole fractions given in Table 1.

Page 19934, Section 3.5 and Table 3. If possible, I would suggest that some estimate of the error associated with these values be calculated and included in the text and/or Table 3.

Page 19934, line 18. How close were the two values calculated for methanol/MAE nucleophilicity prior to averaging?

We have added an estimate for the uncertainties in the relative nucleophilicity values given in Table 3.

Page 19936, line 1,2. Does IEPOX reactivity also increase under more acidic conditions, so that if MAE reactivity were estimated as equal to that of IEPOX, it will now be lower even under conditions of high SOA acidity?

We agree that the parenthetical remark seems to indicate that IEPOX and MAE reactivity would have different acid dependences, which is not the actual expectation. We have removed the parenthetical remark.

Page 19953, Figure 8. It may aid the reader to have a comment in the figure caption defining the species referred to by the labels (‘diester’, ‘triester’, etc.) or referring to the figure where their structures are shown.

We have added a reference to Figure 1 to the caption so that it is clear where the labels are defined.

Minor edits:

Page 19923, line 2: 'for' should be removed from phrase in parentheses

Changed to "as in the case of MAE, the purity was in excess of 95%."

Page 19932, line 28: missing 'the' at the end of the line

Typo corrected.

Page 19934, line 17: missing 'be' between 'can' and 'used'

Typo corrected.

Page 19936, line 13: 'this result leads' or 'these results lead'

Typo corrected.

Page 19937, line 20: missing 'the' before diester

Typo corrected.

1 **Mechanistic study of secondary organic aerosol**  
2 **components formed from nucleophilic addition reactions of**  
3 **methacrylic acid epoxide**

4  
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10  
11 **Abstract**

12 Recently, methacrylic acid epoxide (MAE) has been proposed as a precursor to an important  
13 class of isoprene-derived compounds found in secondary organic aerosol (SOA): 2-  
14 methylglyceric acid (2-MG) and a set of oligomers, nitric acid esters and sulfuric acid esters  
15 related to 2-MG. However, the specific chemical mechanisms by which MAE could form  
16 these compounds have not been previously studied- with experimental methods. In order to  
17 determine the relevance of these processes to atmospheric aerosol, MAE and 2-MG have been  
18 synthesized and a series of bulk solution-phase experiments aimed at studying the reactivity  
19 of MAE using nuclear magnetic resonance (NMR) spectroscopy have been performed. The  
20 present results indicate that the acid-catalyzed MAE reaction is more than 600 times slower  
21 than a similar reaction of an important isoprene-derived epoxide, but is still expected to be  
22 kinetically feasible in the atmosphere on more acidic SOA. The specific mechanism by  
23 which MAE leads to oligomers was identified, and the reactions of MAE with a number of  
24 atmospherically relevant nucleophiles were also investigated. Because the nucleophilic  
25 strengths of water, sulfate, alcohols (including 2-MG), and acids (including MAE and 2-MG)  
26 in their reactions with MAE were found to be of a similar magnitude, it is expected that a  
27 diverse variety of MAE + nucleophile product species may be formed on ambient SOA.  
28 Thus, the results indicate that epoxide chain reaction oligomerization will be limited by the  
29 presence of high concentrations of non-epoxide nucleophiles (such as water); this finding is  
30 consistent with previous environmental chamber investigations of the relative humidity-  
31 dependence of 2-MG-derived oligomerization processes and suggests that extensive



1 oligomerization may not be likely on ambient SOA because of other competitive MAE  
2 reaction mechanisms.

### 3 | 4 **1 Introduction**

5 Due to isoprene's significant contribution to global secondary organic aerosol (SOA) (Carlton  
6 et al., 2009; Hallquist et al., 2009), the atmospheric chemical mechanisms by which this  
7 volatile substance is converted into aerosol phase components have recently received intense  
8 scrutiny. Previous studies using environmental chamber experiments have shown that  
9 isoprene-derived SOA can be formed through an oxidation pathway that begins with  
10 methacrolein, a first-generation product of isoprene oxidation, and results in the formation of  
11 2-methylglyceric acid (2-MG), a compound that has been observed in laboratory-generated  
12 and ambient atmospheric SOA (Surratt et al., 2006; Jaoui et al., 2008; Edney et al., 2005;  
13 Szmigielski et al., 2007; Zhang et al., 2011). Further environmental chamber studies have  
14 established that methacryloylperoxynitrate (MPAN) is a second-generation oxidation product  
15 in this pathway (Surratt et al., 2010).

16  
17 In addition to 2-MG itself, related compounds have also been observed on SOA. In  
18 environmental chamber experiments, oligomers, nitric acid esters, and sulfuric acid esters  
19 structurally related to 2-MG have been characterized using a variety of chromatographic and  
20 mass spectroscopic techniques (Chan et al., 2010a; Surratt et al., 2007; Szmigielski et al.,  
21 2007; Hatch et al., 2011a; Gómez-González et al., 2008; Zhang et al., 2011). In one case, the  
22 observation of a dimer containing two 2-MG subunits connected via an ester linkage in  
23 ambient aerosol has been reported (~~Jaoui et al., 2008~~)([Jaoui et al., 2008](#)). These species are of  
24 particular interest in understanding SOA composition because they possess volatilities even  
25 lower than that of 2-MG, due to increased molecular weights and/or the presence of highly  
26 polar nitrate and sulfate groups.

27  
28 Recent atmospheric chamber experiments suggest that water content (i.e., relative humidity  
29 (RH)) plays a large role in determining the extent of oligomerization of species containing 2-  
30 MG subunits. Under conditions of very low water content (RH<2%), the photooxidation of  
31 isoprene was observed to lead to 2-MG-derived oligoesters up to 8 units in length (Nguyen et  
32 al., 2011). On the other hand, a 69% reduction in 2-MG oligomer formation was observed

1 under high water content (RH=90%) conditions. Similarly, a second investigation of isoprene-  
2 derived SOA found that the extent of 2-MG-derived oligomerization decreased by almost a  
3 factor of 4 as the water content was increased from 13% RH to 88% RH (Zhang et al., 2011).  
4 A third study of methacrolein-derived SOA determined that 2-MG-derived oligomerization  
5 was extensive at <10% RH, with up to five 2-MG units in the oligomers (Chan et al., 2010a).

6  
7 The mechanisms by which sulfate esters, nitrate esters, and oligoesters containing 2-MG are  
8 formed, and the conditions necessary for efficient formation, are currently unknown. One  
9 possible source of these compounds is via acid-catalyzed reactions of 2-MG itself. In  
10 particular, a Fischer esterification mechanism would allow for oligomeric chains of 2-MG to  
11 be formed or for nitrate and sulfate ester formation in the presence of those inorganic ions.  
12 However, previous kinetics measurements suggest that, under the typical range of aerosol  
13 conditions, Fischer esterification of 2-MG proceeds too slowly to account for the extent of  
14 oligomer formation observed in atmospheric chamber experiments (Birdsall et al., 2013).

15  
16 Recent atmospheric chamber studies and field observations have demonstrated that an  
17 epoxide species, methacrylic acid epoxide (MAE), may be, via hydrolysis reaction, the  
18 precursor to 2-MG formation (Lin et al., 2013). Therefore, it is also quite possible that the  
19 various classes of esters containing 2-MG units identified in atmospheric chamber  
20 experiments may also be products of MAE reactions, rather than of reactions solely involving  
21 2-MG. Indeed, in an analogous situation, laboratory studies of isoprene-derived SOA-phase  
22 chemistry (Lin et al., 2012; Surratt et al., 2010; Darer et al., 2011; Hu et al., 2011; Cole-  
23 Filipiak et al., 2010) and field observations of SOA (Hatch et al., 2011b; Surratt et al., 2010;  
24 Chan et al., 2010b) for isoprene-dominated situations have uncovered evidence that many of  
25 the individual isoprene backbone-retaining chemical species observed are the result of the  
26 SOA-phase reactions of isoprene epoxydiols (IEPOX) (Paulot et al., 2009). Therefore, it is of  
27 interest to explore the potential mechanisms by which methacrolein-derived epoxide  
28 intermediates, such as MAE, may lead to the previously observed methacrolein backbone-  
29 containing SOA components (i.e., 2-MG-related species).

30  
31 In this paper, we report measurements of the bulk-phase reaction of MAE with a number of  
32 atmospherically relevant nucleophiles (including MAE itself and 2-MG), using nuclear

1 magnetic resonance (NMR) as the analytic technique. The mechanistic and kinetic data  
2 obtained from these experiments are then used to assess the potential nature of MAE reaction  
3 on ambient SOA.

4

## 5 **2 Experimental**

### 6 **2.1 Synthesis of reactants**

#### 7 **2.1.1 Synthesis of MAE**

8 Both MAE and 2-MG were synthesized following a procedure previously developed to  
9 synthesize 2-MG (Birdsall et al., 2013). All precursor compounds were obtained from Sigma-  
10 Aldrich and used as obtained, with given purities, unless otherwise noted. Methacrylic acid  
11 (MA) (99%, 20 mL, 1 equiv) was added to a 500 mL round-bottom flask containing reagent-  
12 grade dichloromethane (200 mL) and a magnetic stir bar. An excess of *meta*-  
13 chloroperoxybenzoic acid (*m*CPBA) ( $\leq 77\%$ , 55 g, 1.25 equiv) was then added as the oxidant.  
14 Monitoring the reaction progress with  $^1\text{H}$  NMR showed complete epoxidation was achieved  
15 after 7 days of stirring at room temperature (22 °C), or 24 h under reflux (40 °C). After  
16 filtering off excess *m*CPBA (and the oxidation product *meta*-chlorobenzoic acid (*m*CBA))  
17 with successive vacuum filtration and gravity filtration steps until the solution contained no  
18 visible precipitate, the crude, dilute epoxide product was divided into two fractions of equal  
19 volume: one fraction was worked up to provide purified MAE, while in the other fraction, the  
20 MAE was hydrolyzed and isolated to provide 2-MG.

21

22 In order to isolate MAE, further extraction and purification steps were performed, following a  
23 literature procedure (Grill et al., 2006). Complete rotary evaporation of dichloromethane  
24 resulted in a white slurry. The slurry was transferred to a flask with a minimum of cold (0 °C)  
25 deionized water (approximately 40 mL) and briefly swirled by hand. Because MAE is quite  
26 water soluble, it partitioned into the aqueous phase. The remaining solid (presumably *m*CBA)  
27 was removed via consecutive vacuum and gravity filtration steps and discarded. The  
28 remaining aqueous solution underwent rotary evaporation (15 torr pressure, 40 °C bath) until  
29 no further volume loss was observed, resulting in a clear, viscous liquid.

30

1 In part because the  $^1\text{H}$  NMR spectrum revealed that the aqueous extraction resulted in  
2 significant hydrolysis of MAE to 2-MG, MAE was then isolated using flash column  
3 chromatography (~~Costa et al., 2013~~)(Costa et al., 2013) with diethyl ether (Fisher Scientific)  
4 as the eluent. The isolated MAE was confirmed to be >95% pure by  $^1\text{H}$  NMR. Due to the  
5 observed slow self-reaction of MAE at room temperature, MAE was stored at  $-80\text{ }^\circ\text{C}$  when  
6 not in use.

### 7 **2.1.2 Synthesis of 2-MG**

8 2-MG was formed from the other fraction of dilute, crude MAE by simultaneous aqueous  
9 extraction and acid-catalyzed hydrolysis, as described previously (Birdsall et al., 2013). In  
10 some cases, a solid was observed to have precipitated out of the crude MAE solution during  
11 storage. In this case, another gravity filtration was performed before proceeding with the  
12 hydrolysis procedure. The solution was then transferred to an Erlenmeyer flask, and 50 mL of  
13 0.2 M  $\text{HClO}_4$  (prepared from 70%  $\text{HClO}_4$ ) was added to the mixture to form a biphasic  
14 solution with precipitate formation observed in the interfacial region. The solution was stirred  
15 continuously, and if necessary, sparing amounts of additional dichloromethane was added  
16 over time as dichloromethane evaporated in order to maintain two clearly defined phases.  
17 Over 8 days, MAE partitioned into the aqueous phase and hydrolyzed into 2-MG. The  
18 solution was gravity filtered, and the aqueous phase was isolated using a separatory funnel.  
19 The strong acid (i.e.,  $\text{HClO}_4$  but not 2-MG) component of the solution was stoichiometrically  
20 neutralized with NaOH solution (97%, 10 mL, 1.0 M). The dilute 2-MG solution was  
21 transferred to a glass trap with a magnetic stir bar and attached to a vacuum system. Water  
22 was removed by gradually lowering the pressure to <1 torr, with vigorous stirring and  
23 immersion in a water bath maintained at 295 K, until no more volume loss or drop in vacuum  
24 pressure were observed (at approximately 500-600 millitorr). This endpoint was achieved  
25 after approximately 2 h of vacuum pumping. No further purification of the resulting 2-MG  
26 was found to be necessary (as ~~for~~in the case of MAE, the purity was in excess of 95%),  
27 though as discussed in Birdsall et al., (2013), the self-catalyzed conversion of 2-MG via  
28 Fischer esterification to oligomer products was observed to appear with an initial  
29 concentration of 2% and roughly 7% after 6 months of storage at room temperature (295 K).  
30 To avoid even this very slow process, 2-MG was also stored at  $-80\text{ }^\circ\text{C}$  when not in use.

## 1 2.2 NMR technique

2 A variety of nuclear magnetic resonance (NMR) spectra were collected to identify and  
3 quantify the products of reactions of MAE. A 400 MHz Varian NMR spectrometer was used  
4 to collect all spectra, using default experimental parameters except where noted. Built-in auto-  
5 lock and gradient shim routines were used before collecting each spectrum, except when  
6 increased temporal resolution was necessary for kinetics measurements. In these cases, the  
7 auto-lock and gradient shim routines were performed only once, immediately before the first  
8 of a series of spectra were collected. Chemical shifts were calibrated relative to the solvent  
9 HDO peak (4.79 ppm) for all  $^1\text{H}$  spectra, and relative to DSS (0.0 ppm) (or by using  
10 secondary standards that were referenced to DSS) for all  $^{13}\text{C}$  spectra. For experiments  
11 performed in aqueous solution,  $\text{D}_2\text{O}$  (Cambridge Isotope Laboratories) was used as a solvent.  
12 Deuterated methanol,  $\text{CD}_3\text{OD}$ , and deuterated acetic acid  $\text{CD}_3\text{COOD}$  (both Cambridge  
13 Isotope Laboratories) were also used as solvents (and nucleophiles) in some experiments, as  
14 well.

15  
16 The kinetics of MAE hydrolysis were determined using an NMR-based technique previously  
17 developed in our lab (Darer et al., 2011; Birdsall et al., 2013). For these experiments,  $^1\text{H}$   
18 spectra were collected with 8 scans (30 s) which gave a large enough signal-to-noise ratios to  
19 ~~allow for quantitative integration~~ be able to follow MAE reactant loss over more than an order  
20 of magnitude of relative concentration.

21  
22 Product studies of reactions of MAE required the collection of 1D  $^{13}\text{C}$  NMR spectra, as well  
23 as several 2D spectroscopic techniques:  $^1\text{H}$ - $^1\text{H}$  correlation spectroscopy (COSY),  $^1\text{H}$ - $^{13}\text{C}$   
24 Heteronuclear Multiple Quantum Correlation spectroscopy (HMQC), and  $^1\text{H}$ - $^{13}\text{C}$   
25 Heteronuclear Multiple Bond Coherence spectroscopy (HMBC) (Braun et al., 1998). This  
26 suite of NMR experiments provided information about single- and multiple-bond couplings  
27 necessary to determine bond connectivity in product molecules and resolve overlapping peaks  
28 in 1D NMR spectra.

29  
30 Built-in pulse sequences were used for all experiments; an increased number of scans were  
31 often used to enhance the signal-to-noise. COSY spectra were collected using the gDQCOSY

1 pulse sequence, which includes both a double-quantum filter and a gradient pulse for  
2 improved signal and fewer artifacts. The pulse sequences used to collect HMQC and HMBC  
3 spectra, gHMQC and gHMBCAD, respectively, both contained a gradient pulse as well, while  
4 the gHMBCAD sequence also included an adiabatic pulse. When necessary to enhance the  
5 resolution and signal of HMBC and HMQC spectra, the number of increments and  
6 scans/increment were increased from the defaults, up to a maximum of 1024 increments and  
7 32 scans/increment. For experiments querying carbon atoms (1D  $^{13}\text{C}$  NMR, HMBC), the  
8 spin-lattice relaxation time (T1) was increased when necessary, from 1 s to 2-10 s, to improve  
9 the signal strength of quaternary carbon peaks.

### 10 **2.3 MAE hydrolysis kinetics**

11 The kinetics of MAE hydrolysis was measured by using  $^1\text{H}$  NMR to monitor the hydrolysis of  
12 MAE to 2-MG of solutions containing known amounts of MAE, water, and acid. For each  
13 hydrolysis kinetics experiment, 10  $\mu\text{L}$  of MAE was dissolved in 990  $\mu\text{L}$  of 0.10-1.0 M  $\text{D}_2\text{SO}_4$   
14 in  $\text{D}_2\text{O}$  in a 10 mL beaker, with stirring, for 2-3 min. The 1 mL solution was then transferred  
15 to a 5 mm NMR tube and  $^1\text{H}$  spectra were collected as the hydrolysis progressed, with the  
16 time intervals between spectral collection adjusted according to the rate of the reaction.

### 17 **2.4 MAE nucleophilic addition product identification and relative nucleophilicity** 18 **determination methods**

#### 19 **2.4.1 Deuterated solvent nucleophiles/direct NMR analysis method**

20 For the cases where deuterated nucleophiles were available, MAE was added to the deuterated  
21 nucleophile solutions and the reaction was directly monitored in the NMR tube in a process  
22 very similar to the method used for the hydrolysis kinetics study.

23

24 Three experimental solutions were prepared (the compositions of the various solutions are  
25 given in Table 1): To assess the relative nucleophilicity of sulfate and water in their reactions  
26 with MAE, a solution consisting of 10  $\mu\text{L}$  of MAE and 600  $\mu\text{L}$  of 1 M  $\text{D}_2\text{SO}_4$  in  $\text{D}_2\text{O}$  was  
27 prepared (experiment #1). To assess the relative nucleophilicity of acetic acid and water in  
28 their reactions with MAE, a solution consisting of 10  $\mu\text{L}$  of MAE and 1000  $\mu\text{L}$  of an  
29 equimolar  $\text{CD}_3\text{COOD}/\text{D}_2\text{O}$  solution was prepared (experiment #2). To assess the relative

1 nucleophilicity of acetic acid and methanol in their reactions with MAE, a solution consisting  
2 of 50  $\mu\text{L}$  of MAE and 1000  $\mu\text{L}$  of an equimolar  $\text{CD}_3\text{COOD}/\text{CD}_3\text{OD}$  solution was prepared  
3 (experiment #3). Upon the addition of MAE, the solutions were stirred for 2-3 min, at which  
4 point the samples were transferred to 5 mm NMR tubes and spectra were collected.

#### 5 **2.4.2 Normal isotope nucleophiles/aliquot NMR analysis method**

6 For the cases where deuterated nucleophiles were not available, MAE was added to the  
7 normal isotope nucleophile solution, stirred for 2-3 minutes, and the reaction mixture was  
8 stored in a vial at room temperature. Small volume aliquots of these solutions were  
9 periodically withdrawn from the vials, added to about 700  $\mu\text{L}$  of  $\text{D}_2\text{O}$ , and the resulting  
10 mixtures were loaded into NMR tubes and spectra were collected.

11  
12 Four experimental solutions (Table 1) were prepared: To assess the potential oligomer  
13 forming reactions of MAE, a neat MAE sample was monitored (experiment #4). To assess  
14 the relative nucleophilicity of MAE and 2-MG in their reactions with MAE, a solution  
15 consisting of 50  $\mu\text{L}$  of MAE and 0.551 g of 2-MG was prepared (experiment #5). To assess  
16 the relative nucleophilicity of MAE and water in their reactions with MAE, a solution  
17 consisting of 300  $\mu\text{L}$  of MAE and 29  $\mu\text{L}$  of water (a 2:1 MAE/ $\text{H}_2\text{O}$  molar ratio) was prepared  
18 (experiment #6). To assess the relative nucleophilicity of 2-MG and methanol in their  
19 reactions with MAE, a solution consisting of 40  $\mu\text{L}$  of MAE and 0.788 g of an equimolar 2-  
20 MG/ $\text{H}_2\text{O}$  solution that had a small amount of methanol added (the actual methanol content of  
21 the solution was determined via NMR methods) was prepared (experiment #7).

22

### 23 **3 Results**

#### 24 **3.1 MAE and 2-MG NMR identification**

25  $^1\text{H}$  NMR peak assignments for the species observed in the MAE hydrolysis experiments were  
26 consistent with the MAE assignments (Lin et al., 2013) and 2-MG assignments (Birdsall et  
27 al., 2013) previously reported. As discussed in the Supplement to Birdsall et al., 2013, sets of  
28 peaks postulated to arise from diastereomers were observed in the  $^1\text{H}$  and  $^{13}\text{C}$  spectra in a  
29 manner that is consistent with the observations of Espartero et al. (1996) for similar lactic  
30 acid-derived species. The complete  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift assignments for MAE and 2-  
31 MG are given in Figures 1 and 2, respectively.

### 3.2 MAE hydrolysis kinetics

The rate-determining step of acid-catalyzed epoxide hydrolysis is typically the opening of the epoxide ring, preceded by protonation of the epoxide that acts as a pre-equilibrium step. Because of this pre-equilibrium, the differential rate law for this reaction can be written in terms of its dependence on  $H^+$  and MAE

$$-\frac{d[MAE]}{dt} = k[H^+][MAE] \quad (1)$$

where  $k$  is the rate constant, and  $[MAE]$  and  $[H^+]$  are the molar concentrations of MAE and  $H^+$ , respectively. Since the actual acid does not also act as a catalyst/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 as 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). Thus, from Eq. 1 and 2 the integrated pseudo-first order rate law is obtained,

$$\ln \frac{[MAE]}{[MAE]_0} = -k't \quad (3)$$

where  $[MAE]_0$  is the initial concentration of MAE. Fig. 3 provides a sample plot of  $\ln \frac{[MAE]}{[MAE]_0}$  as a function of time, using the relative integrated areas of the methylene protons of 2-MG and MAE in  $^1H$  NMR spectra to calculate  $[MAE]/[MAE]_0$ .

The bimolecular rate constant is determined from the extracted  $k'$  values over a range of acid concentrations, using the relationship in Eq. 2 (Fig. 4). The range of acidities accessible to our experiments was bounded on the lower end by the increasing significance of the presence of trace sources of acidity (postulated to arise from MAE/2-MG), and on the upper end by the susceptibility of sulfate ester formation at high sulfuric acid concentrations. The extracted rate



1 constant  $k$  (and one standard deviation statistical error) was found to be  $5.91 \pm 0.45 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ .  
2 Due to possible kinetic isotope effects, the presently reported rate constant (measured in  
3 deuterated solvent conditions) may differ from the rate constant appropriate for aerosol  
4 environments (normal isotope solvent conditions). While this effect was not investigated in  
5 the present study, a previous acid-catalyzed epoxide kinetics investigation (Eddingsaas et al.,  
6 2010) estimated that deuterated solvent conditions lead to rate constants that are either equal  
7 to those for normal isotope solvent conditions (for  $\text{SN}_2$ -like mechanisms) to rate constants as  
8 much as a factor of two larger than for normal isotope solvent conditions (for  $\text{SN}_1$ -like  
9 mechanisms).

10  
11 The newly obtained rate constant for MAE hydrolysis can be compared to previously  
12 published structure-reactivity trends in bulk phase epoxide hydrolysis kinetics for molecules  
13 with alcohol groups (Cole-Filipiak et al., 2010; Minerath et al., 2009). In general, it was found  
14 that hydroxyl substitution on a carbon atom adjacent to the epoxide ring reduced the  
15 hydrolysis rate constant by up to three orders of magnitude, presumably due to inductive  
16 effects that destabilize the carbocation intermediate.

17  
18 Table 2 compares the rate constant for MAE hydrolysis to those of other structurally similar  
19 epoxides and/or atmospherically relevant epoxides. The epoxide without hydroxyl or carboxyl  
20 substitution, 2-methyl-1,2-epoxypropane, has the largest rate constant of all species. The  
21 hydroxyl-substituted species, 3-methyl-3,4-epoxy-1,2-butanediol (IEPOX-1) and 2-methyl-  
22 2,3-epoxy-1,4-butanediol (IEPOX-4) have rate constants 2-3 orders of magnitude smaller, in  
23 line with the predicted structure-reactivity relationship. On the other hand, the carboxyl-  
24 substituted species, MAE, has a rate constant more than 600 times smaller than the  
25 atmospherically relevant IEPOX-4 species. A recent computational study has predicted that  
26 MAE hydrolysis will proceed at a rate 1700 times slower than IEPOX-4 (Piletic et al., 2013),  
27 a result in good agreement with the present experimental finding. The computational study  
28 also suggested that the reason for the large difference in reactivity is due to a fundamental  
29 difference in reaction mechanism: while IEPOX-4 primarily undergoes nucleophilic attack at  
30 its tertiary epoxide carbon atom, the computational work suggested that MAE will primarily  
31 undergo nucleophilic reaction at its primary epoxide carbon atom.

### 3.3 Identification of nucleophilic addition mechanisms for MAE reacting with sulfate, methanol, and acetic acid

Figure 5 depicts the two possible generic nucleophilic addition pathways for MAE, one leading to a tertiary addition product, which was not observed in any case, and one leading to a primary addition product, which was observed in every case. For clarity concerning the position of nucleophilic addition, these mechanisms are drawn as sequential reaction ( $\text{SN}_1$ -like) mechanisms. While it is likely that these mechanisms are more accurately represented by concerted ( $\text{SN}_2$ -like) formalism, the actual mechanism may lie somewhere on a continuum between the sequential and concerted pathways (Whalen, 2005; Eddingsaas et al., 2010; Piletic et al., 2013). It should be noted, however, that the preceding hydrolysis kinetics analysis does not depend on the actual mechanistic pathway (since nucleophilic water is in excess and has an unchanging concentration in those experiments, the two mechanisms are experimentally indistinguishable). Since 2-MG has both alcohol and carboxylic acid functional groups that could potentially act as nucleophiles, methanol and acetic acid were chosen as model systems to explore the similarities and differences for these two different types of nucleophiles. In addition, MAE + sulfate was studied, as 2-MG-related sulfate esters have been identified in previous atmospheric chamber experiments (Gómez-González et al., 2008; Surratt et al., 2007; Hatch et al., 2011a). The NMR evidence for the exclusive presence of a primary addition product for all three nucleophiles - methanol, acetic acid, and sulfate - is discussed in detail below.

#### 3.3.1 MAE + sulfate reaction

This reaction was carried out in a 1 M  $\text{D}_2\text{SO}_4$  solution (experiment #1), with sulfuric acid serving as both the source of the nucleophilic sulfate ions ( $[\text{SO}_4^{2-}] = 0.75 \text{ M}$  according to the Extended Aerosol Inorganics Model (E-AIM) (Clegg et al., 1998)) and the source of acidity ( $[\text{D}^+] = 1.2 \text{ M}$  according to E-AIM) needed for catalysis. The relatively fast observed product-forming kinetics indicated that the sulfate ester product was forming as the result of fast MAE +  $\text{SO}_4^{2-}$  reaction as opposed to slow Fischer esterification 2-MG +  $\text{SO}_4^{2-}$  reaction (Birdsall et al., 2013). To determine which epoxide carbon the sulfate group had attacked (the two nucleophilic addition pathways shown in Figure 5), the  $^1\text{H}$  chemical shifts of the sulfate species was compared to those of 2-MG. The relative  $\text{CH}_3$  and  $\text{CH}_2$  shifts of the sulfate ester compared to those of 2-MG ( $\sim 0.4 \text{ ppm}$  downfield) are the same as the Fischer esterification-

1 produced sulfate ester observed by Birdsall et al., 2013, which was determined through  
2 analysis of  $^{13}\text{C}$  NMR spectra to be the primary sulfate. Furthermore, based on previous work  
3 with sulfates structurally related to 1,2,3,4-butanetetrol, the  $^1\text{H}$  NMR spectrum of the tertiary  
4 sulfate would be expected to differ significantly, with the  $\text{CH}_2$  peaks in the MAE-derived  
5 tertiary sulfate expected to appear 0.1 to 0.2 ppm downfield of the 2-MG  $\text{CH}_2$  peaks  
6 (Minerath and Elrod, 2009). Such peaks were not observed, and thus the NMR evidence  
7 points to the exclusive formation ( $< 0.5\%$  of initial MAE reactant amount) of a primary  
8 sulfate addition product. As discussed in Section 3.2, a previous computational study has  
9 identified the primary addition mechanism as the more kinetically facile pathway (Piletic et  
10 al., 2013), a finding quite consistent with the present experimental results. The complete  $^1\text{H}$   
11 and  $^{13}\text{C}$  chemical shift assignments for this species are given in Figures 1 and 2, respectively.

### 12 **3.3.2 MAE + methanol reaction**

13 In the methanol nucleophile experiments, either  $\text{CD}_3\text{COOD}$  (experiment #3) or 2-MG  
14 (experiment #7) provided the acidity needed for the catalysis of the reaction. For the  
15 experiment using  $\text{CD}_3\text{OD}$  (experiment #3), new peaks ([at 3.45 and 3.75 ppm](#)) located near the  
16 2-MG peaks ([at 3.60 and 3.82 ppm](#)) were observed, consistent with the formation of a single  
17 ether isomer from the nucleophilic addition of methanol to MAE. However, in order to  
18 establish the nucleophilic attack position of the methanol moiety, it was also useful to  
19 investigate the spectra of the normal isotope (experiment #7). In particular, having  
20 observable protons in the  $^1\text{H}$  NMR spectrum from the nucleophilic methanol species allowed  
21 for long-range coupling between the added methanol moiety and the carbon atom that it  
22 attacked in the MAE moiety to be observed. This long-range coupling, observable in an  
23 HMBC spectrum, allowed for the definitive structural assignment of a primary or tertiary  
24 nucleophilic attack product to be made. In particular, the HMBC spectrum showed a single 3-  
25 bond coupling between the protons on the methanol moiety and primary carbon atom on the  
26 MAE moiety. Had the tertiary addition product formed, a 3-bond coupling between the  
27 protons on the methanol moiety and the tertiary carbon would have been observed in the  
28 HMBC spectrum. Therefore, as for the sulfate addition case, the NMR spectrum indicates the  
29 sole formation of a methanol primary addition product. The complete  $^1\text{H}$  and  $^{13}\text{C}$  chemical  
30 shift assignments for this species are given in Figures 1 and 2, respectively.

### 1 3.3.3 MAE + acetic acid system

2 In the acetic acid nucleophile experiments, CD<sub>3</sub>COOD provided the acidity needed for the  
3 catalysis of the reaction. Once again, the NMR evidence showed that the single primary  
4 addition species was the sole product formed. The partial <sup>1</sup>H and <sup>13</sup>C chemical shift  
5 assignments for this species are given in Figures 1 and 2, respectively (the acetic acid moiety  
6 proton and carbon atoms were not observed due to the exclusive use of CD<sub>3</sub>COOD). In the  
7 MAE + CD<sub>3</sub>COOD/D<sub>2</sub>O experiment (experiment #2), the actual pH of the solution could be  
8 calculated from the initial concentrations and the known pK<sub>a</sub> of acetic acid (pH = 1.8). If the  
9 reaction were following a sequential S<sub>N1</sub>-like mechanism (in which the nucleophile  
10 concentration does not affect the overall rate of the reaction), the formal second order rate  
11 constant would be expected to be identical to the value determined in the hydrolysis  
12 experiment. On the other hand, if the reaction were following a concerted S<sub>N2</sub>-like  
13 mechanism, the phenomenological second order rate constant would be expected to larger  
14 if acetic acid were a stronger nucleophile than water, and smaller if acetic acid were a weaker  
15 nucleophile than water. The actual second order rate constant determined from experiment #2  
16 was 5.0 x 10<sup>-5</sup> M<sup>-1</sup> s<sup>-1</sup>. Since this value is within the experimental uncertainty of the  
17 hydrolysis rate constant, an S<sub>N1</sub>-type mechanism cannot be ruled out. On the other hand,  
18 assuming an S<sub>N2</sub>-type mechanism, this slightly smaller rate constant could be interpreted as  
19 indicating that acetic acid is a somewhat weaker nucleophile than water. However, since the  
20 reaction may actually be operating along a continuum between the S<sub>N1</sub>- and S<sub>N2</sub>-like  
21 mechanisms, it is quite difficult to draw any definitive conclusions from this result.

### 22 3.4 Identification of nucleophilic addition mechanisms for MAE reacting with 23 MAE and 2-MG

24 Based on the demonstrated preference for MAE to react at its primary epoxide carbon (as  
25 outlined above in Section 3.3), it was assumed, as a preliminary analysis provision, that the  
26 nucleophiles MAE and 2-MG will also attack exclusively at the MAE primary carbon. Figure  
27 6 depicts the specific nucleophilic addition of one MAE molecule acting as a nucleophile  
28 (through the OH group on its carboxylic acid moiety) to another MAE molecule. This  
29 particular mechanism is capable of producing the kind of higher order oligomers (via chain  
30 reaction of the epoxy ester products with MAE) observed in previous environmental chamber  
31 studies (Zhang et al., 2011; Chan et al., 2010a; Nguyen et al., 2011). Figure 7 depicts the  
32 three possible specific nucleophilic addition options for a 2-MG molecule attacking MAE. If

1 2-MG uses its carboxylic acid OH group, a primary diester (a molecule in which two 2-MG  
2 subunits are connected via a single ester linkage) would be expected to form (this particular  
3 species can also be produced via the acid-catalyzed Fischer self-esterification of 2-MG, a  
4 process previously studied in our lab (Birdsall et al., 2013)). On the other hand, if 2-MG uses  
5 either of its alcoholic OH groups, either a primary or a tertiary diether (molecules in which  
6 two 2-MG subunits are connected via a single ether linkage) would be expected to form. The  
7 nomenclature used to identify the various species in Figures 1,2,6 and 7 is intended to  
8 highlight the mechanistic route by which the species formed. For example, the *primary*  
9 *diester* name assigned to the species formed as shown at the bottom of Figure 7 reflects that  
10 this dimeric species (formed from the reaction of MAE with 2-MG) is connected via a single  
11 ester linkage that formed at the *primary* epoxide carbon of MAE.

12

13 For the MAE + MAE reaction (experiment #4), MAE provided the acidity needed for the  
14 catalysis of the reaction, while in the MAE + 2-MG reactions (experiments #5 and #7), 2-MG  
15 provided the acidity. Due to the presence of unavoidable water impurity in the MAE sample,  
16 the "neat" MAE reaction system (experiment #4) is actually the most complicated one, since  
17 MAE can react with itself, water, 2-MG (formed from reaction of MAE with water), which  
18 were all present in significant concentrations in experiment #4 (indeed, some of the products  
19 of these reactions were identified as participating in further reactions further adding to the  
20 number of observed species). However, with the aid of experiments in which the relative  
21 MAE:water:2-MG amounts were changed (experiments #5 and #6), all of the various  
22 products were identified and quantified. The carbonyl region of the <sup>13</sup>C NMR spectrum for  
23 experiment #4 is shown in Figure 8 for the two conditions of early reaction (most MAE is still  
24 unreacted) and late reaction (most MAE has reacted). During the early phase of the reaction,  
25 both the epoxy diester and 2-MG are observed products: 2-MG is formed via hydrolysis from  
26 the water impurity in the neat MAE sample, while the epoxy diester is formed from the MAE  
27 + MAE mechanism shown in Figure 5. During the late reaction phase, the epoxy triester is  
28 observable (formed from the reaction of the epoxy diester + MAE, as shown in Figure 6), in  
29 addition to two of the species shown in Figure 7: the primary diether species (formed from  
30 MAE reaction with the primary OH group acting as a nucleophilic group on 2-MG) and the  
31 primary diester species. The triester (formed from the reaction of the epoxy diester with 2-  
32 MG) is also evident in the late reaction phase spectrum. The tertiary diether species was not

1 observed (were it present in the NMR spectrum, it could be easily distinguished from the  
2 primary diether because of its asymmetric structure).

3  
4 Since the diester species could be formed from either 1) MAE reaction with the carboxylic  
5 acid OH of 2-MG (as shown in Figure 7) or from 2) hydrolysis of the epoxy diester (as  
6 shown in Figure 9), further experiments were necessary to identify the relevant mechanisms.  
7 In order to isolate the MAE + 2-MG (carboxylic acid nucleophile) diester-forming pathway  
8 and to measure the relative nucleophilicity of 2-MG using its carboxylic acid moiety vs.  
9 alcohol moiety, an experiment was performed in which 2-MG was placed in excess over the  
10 water impurity (experiment #5). Based on NMR quantitation, it was found that the MAE + 2-  
11 MG (carboxylic acid nucleophile) and MAE + 2-MG (alcohol nucleophile) reaction pathways  
12 are equally facile (of the total 0.19 mole fraction MAE + 2-MG products, 0.10 mole fraction  
13 was attributable to the diester product and 0.09 mole fraction was attributable to the diether  
14 product). In experiment #6, additional water was intentionally added to favor the formation  
15 of the diester via the hydrolysis of the epoxy diester species. NMR quantitation for this  
16 experiment indicated that while 0.03 mole fraction of the diether formed (via the MAE + 2-  
17 MG (alcohol nucleophile) pathway), 0.24 mole fraction of the diester formed. Since  
18 experiment #5 indicated that the MAE + 2-MG (carboxylic acid nucleophile) pathway is  
19 expected to produce the diester in the same amounts as the diether, it can be assumed that the  
20 extra 0.21 mole fraction of diester formed in experiment #6 is due to the hydrolysis of the  
21 epoxy diester. Therefore, it is quite likely that the diester product observed in experiment #4  
22 (and identified in Figure 8) is produced from both the MAE + 2-MG (carboxylic acid  
23 nucleophile) and the epoxy diester + H<sub>2</sub>O reactions.

24  
25 While the NMR spectra of the diester were previously reported in the context of the acid-  
26 catalyzed Fischer esterification of 2-MG (Birdsall et al., 2013), the newly observed epoxy  
27 diester and the primary diether species were definitively assigned by using experimental  
28 conditions which favored their formation (experiments #4 and #5, respectively), and with the  
29 aid of HMQC and HMBC correlation experiments. (These experiments also confirmed that all  
30 species were the result of nucleophilic attack on the MAE primary carbon, as expected.) The  
31 complete <sup>1</sup>H and <sup>13</sup>C chemical shift assignments for these species are given in Figures 1 and

1 2, respectively. Due to spectral overlap complications, complete triester and epoxy triester  
2 assignments were not obtained.

3

### 4 **3.5 Relative nucleophilicity scale**

5 Using the initial nucleophilic reactant mole fractions ( $X$ , determined via volume and/or mass  
6 measurements) and the final nucleophilic addition product mole fractions ( $Y$ , determined via  
7 NMR quantiation methods) listed in Table 1, it is possible to determine the relative  
8 nucleophilicities (on a molar basis) for the reaction of MAE with the various nucleophiles via  
9 Equation 4:

$$\frac{\text{nucleophile 1 strength}}{\text{nucleophile 2 strength}} = \frac{(Y_{nuc\ 1}/X_{nuc\ 1})}{(Y_{nuc\ 2}/X_{nuc\ 2})} \quad (4)$$

10

11 Note that in some of the experiments, more than two nucleophiles were present (which is why  
12 the mole fractions in Table 1 don't necessarily sum to unity). It is further possible to relate  
13 the nucleophilic strength of all nucleophiles to that of MAE. Starting with experiments #5  
14 and #6, the relative nucleophilic strengths of 2-MG and water to MAE are established (1.2  
15 and 1.6, respectively). Next, the nucleophilic strengths (relative to MAE) of the other  
16 nucleophiles are established via their strengths relative to 2-MG and water. In the case of  
17 methanol, there are two experiments which can be used to calculate the relative  
18 methanol/MAE nucleophilicity; in this case an average value is calculated. Table 2 gives the  
19 relative nucleophilic strengths of all studied nucleophiles in their reactions with MAE. In a  
20 previous computational study of MAE reactivity, it was predicted that the MAE relative (to  
21 water) nucleophilicities for  $\text{SO}_4^{2-}$  and propanol were 9.8 and 3.6, respectively (Piletic et al.,  
22 2013). Converting the values given in Table 1 to nucleophilicities relative to water for  
23 comparison purposes, the experimental nucleophilicities for  $\text{SO}_4^{2-}$  and methanol were  
24 determined to be 11 and 3.1, respectively, which are in good agreement with the  
25 computational predictions. Interestingly, while the relative nucleophilicity of 2-MG using its  
26 carboxylic acid moiety was experimentally found to be similar to that of acetic acid, the  
27 experimental relative nucleophilicity of 2-MG using its alcohol moiety was found to be  
28 significantly less than methanol. Therefore, while the experimental results indicate that the  
29 nucleophilicity of multifunctional molecules like 2-MG may be approximately viewed as the

1 sum of the nucleophilic strength of separate nucleophilic functional groups, the results also  
2 indicate that caution should be used in this simplifying approach.

3

#### 4 **4 Atmospheric implications**

##### 5 **4.1 MAE reaction feasibility on SOA**

6 Using a previously described framework to estimate the kinetics feasibility of acid-catalyzed  
7 epoxide reactions on SOA (Cole-Filipiak et al., 2010), the lifetime,  $\tau$ , of MAE reaction over a  
8 range of atmospherically relevant pHs was calculated using the equation

$$\tau = [H^+]^{-1}k^{-1} \quad (5)$$

9

10 Using the newly determined experimental MAE reaction rate constant results, Equation 5  
11 yields lifetimes of  $2.0 \times 10^3$  days at pH = 4.0, 6.2 days at pH = 1.5, and 0.20 days at pH = 0.  
12 Thus, over a range of atmospherically relevant pHs (Zhang et al., 2007), the expected lifetime  
13 of MAE reaction can range above and below the average lifetime of an aerosol particle (on  
14 the order of 2 days). The finding that MAE reaction is kinetically feasible under  
15 atmospherically relevant conditions is consistent with the observation of both the hydrolysis  
16 product, 2-MG, and—as reported more recently in Lin et al., 2013—the reactant, MAE, on  
17 ambient SOA. ~~However, the MAE reaction is much slower than that of the atmospherically~~  
18 ~~relevant IEPOX 4 species (by a factor of 620, Table 2). While the MAE reaction route to~~  
19 ~~oligomers was found to be about 30 times faster than the Fischer esterification route~~  
20 ~~previously investigated (Birdsall et al., 2013), the MAE reaction is much slower than that of~~  
21 ~~the atmospherically relevant IEPOX-4 species (by a factor of 620, Table 2).~~ A previous  
22 atmospheric modeling study of the role of IEPOX and MAE assumed, in the absence of  
23 experimental data, that the rate constants for the two species were identical (Pye et al., 2013).  
24 Clearly, the much smaller rate constant for MAE will need to be included in future modeling  
25 efforts, with the result that modeled MAE reactivity will likely be reduced ~~(except for~~  
26 ~~conditions of high SOA acidity).~~

##### 27 **4.2 MAE oligomerization mechanism on SOA**

28 In previous work (Lin et al., 2013), it had been shown that MAE reactions on SOA are  
29 capable of producing the kind of 2-MG subunit-containing oligomers identified in



1 environmental chamber experiments (Zhang et al., 2011; Chan et al., 2010a; Nguyen et al.,  
2 2011). In this work, we have identified the specific mechanism (epoxy ester chain reaction,  
3 as given in Fig. 6) by which MAE reactions lead to such oligomers. While there are  
4 potentially two reaction sites for this oligomerization reaction on the epoxide reactant (the  
5 primary or tertiary carbon), this work has shown that MAE appears to exclusively react via its  
6 primary carbon atom with all studied nucleophiles (including the MAE unit acting as the  
7 nucleophile in the oligomerization chain reaction). Therefore, this ~~results~~ result leads to the  
8 prediction that each higher order oligomer will consist of a single isomer, possessing an  
9 extended open chain structure, owing to the exclusive primary reaction site mechanism.

#### 10 **4.3 MAE nucleophilic reactions on SOA**

11 The products and nucleophilic strengths of a number of MAE + nucleophile reactions were  
12 determined in order to assess the likelihood of MAE reaction with a number of  
13 atmospherically-relevant nucleophilic classes of species: HOH, ROH, RC(=O)OH and sulfate.  
14 The product studies confirmed that MAE can react with each of the classes to form diol, ether,  
15 diester, and sulfate ester species, respectively. This work also showed that 2-MG, a  
16 dihydroxy acid, can react using both its primary alcoholic OH (to form an ether product) and  
17 carboxylic OH (to form an ester product) groups as nucleophilic agents. The measured  
18 relative nucleophilic strengths of the MAE reaction with the various species indicates that  
19 MAE itself is not a particularly strong nucleophile. Thus, it is then straightforward to  
20 rationalize why extensive oligomerization has been observed only for laboratory experiments  
21 under conditions of low SOA water content: at high SOA water content, water successfully  
22 competes with MAE as a nucleophile, and limits oligomerization by direct hydrolysis of MAE  
23 or by hydrolysis of the epoxy diester species (as shown in Fig. 9) that is one of the chain  
24 carriers in the oligomerization chain reaction. In ambient SOA, other effective nucleophiles  
25 may be present in high concentrations (such as alcohols, acids, and inorganic ions), and MAE  
26 reactions with these species could also be competitive with hydrolysis and/or oligomerization  
27 mechanistic pathways. Therefore, the nature of MAE reaction on SOA is expected to depend  
28 sensitively on the chemical composition of the preexisting SOA particle; for cases with  
29 heterogeneous SOA compositions, a variety of MAE-derived products may be expected, with  
30 these reactions likely outcompeting the oligomerization pathways (due to MAE's mediocre  
31 nucleophilic strength and relatively low concentration compared to such abundant  
32 nucleophiles such as water and sulfate). While the nitrate nucleophile was not directly

1 studied in these experiments, because its relative nucleophilicity has been found to be similar  
2 to sulfate for reactions with isoprene-derived epoxides (Darer et al., 2011), it is expected that  
3 for MAE reactions that sulfate and nitrate would have similarly nucleophilicities. While

4 hetero-oligomers, formed from cross reactions of MAE with other atmospherically relevant  
5 epoxides (such as IEPOX and 2-methyl-3-buten-2-ol-derived (Zhang et al., 2014) epoxides),  
6 might be formed on ambient SOA, these epoxides are also expected to have mediocre  
7 nucleophilic strength (they are probably more similar to 2-MG than to methanol) and these  
8 reactions would also probably not be competitive with reactions involving more abundant  
9 nucleophiles. Thus far, field studies have identified only two likely MAE reaction products,  
10 2-MG and the diester (Jaoui et al., 2008)(Jaoui et al., 2008), which are likely formed from  
11 hydrolysis of MAE and the reaction of MAE with 2-MG, respectively. The formation of the  
12 diester from the epoxy diester hydrolysis reaction on ambient SOA is less likely since  
13 conditions favoring hydrolysis would also favor the formation of 2-MG, which would  
14 probably lead to the dominance of the MAE + 2-MG diester-forming pathway.

## 15 16 **5 Conclusions**

17 The present results suggest that acid-catalyzed nucleophilic addition to MAE is much slower  
18 than the analogous IEPOX-4 reaction, but, nonetheless, is expected to be kinetically feasible  
19 in the atmosphere, particularly on more acidic SOA. The specific mechanism by which  
20 MAE leads to oligomers was identified (epoxide chain reaction), and the reactions of MAE  
21 with a number of atmospherically relevant nucleophiles were also investigated. Because the  
22 nucleophilic strengths of water, sulfate, alcohols (including 2-MG), and acids (including  
23 MAE and 2-MG) in their reactions with MAE were found to be of a similar magnitude, it is  
24 expected that a diverse variety of MAE + nucleophile product species may be formed on  
25 ambient SOA. Thus, the results indicate that epoxide chain reaction oligomerization will be  
26 limited by the presence of high concentrations of non-epoxide nucleophiles (such as water);  
27 this finding is consistent with previous environmental chamber investigations of the relative  
28 humidity-dependence of 2-MG-derived oligomerization processes and suggests that  
29 ~~extensive oligomerization~~ extensive oligomerization may not be likely on ambient SOA  
30 because of other competitive MAE reaction mechanisms..

## 31 32 **Acknowledgements**

33 This work was supported by the National Science Foundation under Grant No. 1153861.

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1 **Table 1.** Initial reactants mole fractions (X) and final products mole fractions (Y) for the  
 2 different experiments performed. The product mole fractions were determined with an  
 3 estimated relative error of 25%

4

Exp.	X <sub>MAE</sub>	Nuc 1	X <sub>Nuc1</sub>	Nuc 2	X <sub>Nuc2</sub>	Y <sub>MAE-MAE</sub>	Y <sub>MAE-Nuc1</sub>	Y <sub>MAE-Nuc2</sub>
1	0.003	SO <sub>4</sub> <sup>2-</sup>	0.0045	D <sub>2</sub> O	0.992		0.05	0.95
2	0.005	d- AAA A <sup>a</sup>	0.492	D <sub>2</sub> O	0.492		0.28	0.72
3	0.026	d-AA	0.487	d- MeOHM eOH <sup>b</sup>	0.487		0.16	0.84
4 <sup>c</sup>	1.000 ≥ 0.8							
5	0.110	2-MG	0.890			0.02	0.19	
6	0.670	H <sub>2</sub> O	0.330			0.33	0.26	
7	0.021	2-MG	0.461	MeOH	0.054		0.09	0.06

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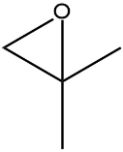
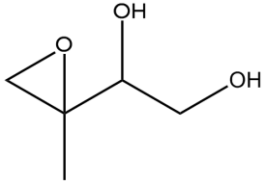
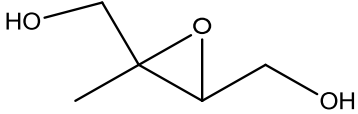
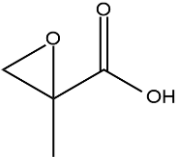
6 <sup>a</sup>d-AA: deuterated acetic acid (CD<sub>3</sub>COOD)

7 <sup>b</sup>d-MeOH: deuterated methanol (CD<sub>3</sub>OD)

8 <sup>c</sup>Experiment #4 was a "neat" sample of MAE contaminated with at most 0.20 mole fraction  
 9 water. Because of the uncertainty in the water content of this sample, Experiment #4 was not  
 10 used in the quantitative determination of relative nucleophilities, but rather was used to  
 11 establish NMR assignments and to aid in the mechanistic interpretation of the MAE reactions.

1 **Table 2.** Acid-catalyzed rate constants for primary-tertiary epoxide hydrolysis with varying  
 2 substitution. <sup>a</sup>(Minerath and Elrod, 2009) <sup>b</sup>(Cole-Filipiak et al., 2010) <sup>c</sup>This work.

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 4  
 5

epoxide	k (M <sup>-1</sup> s <sup>-1</sup> )
 2-methyl-1,2-epoxypropane	8.7 <sup>a</sup>
 IEPOX-1 (3-methyl-3,4-epoxy-1,2-butanediol)	0.0079 <sup>b</sup>
 IEPOX-4 (2-methyl-2,3-epoxy-1,4-butanediol)	0.036 <sup>b</sup>
 MAE (2-methyl-2,3-epoxypropanoic acid)	0.0000591 <sup>c</sup>

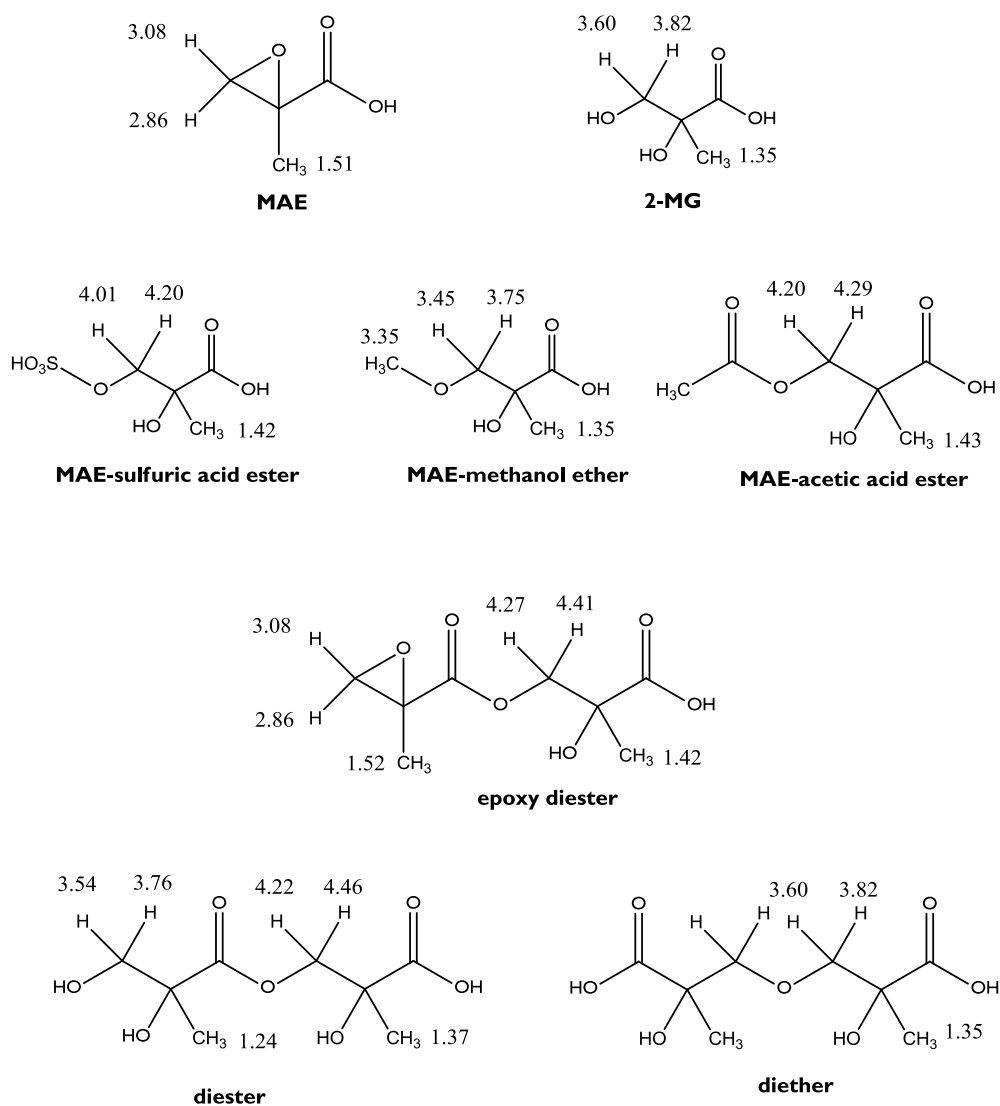
1 | **Table 3.** MAE reaction relative nucleophilic strength scale. The relative nucleophilicities  
2 | were determined with an estimated uncertainty of about 50%, due to uncertainties in both  
3 | reactant and product mole fraction measurements.

4

nucleophile	relative nucleophilicity
acetic acid	0.6
MAE	1 (by definition)
2-MG	1.2 total = 0.6 (carboxylic acid) + 0.6 (primary alcohol)
water	1.6
methanol	5.0
SO <sub>4</sub> <sup>2-</sup>	18

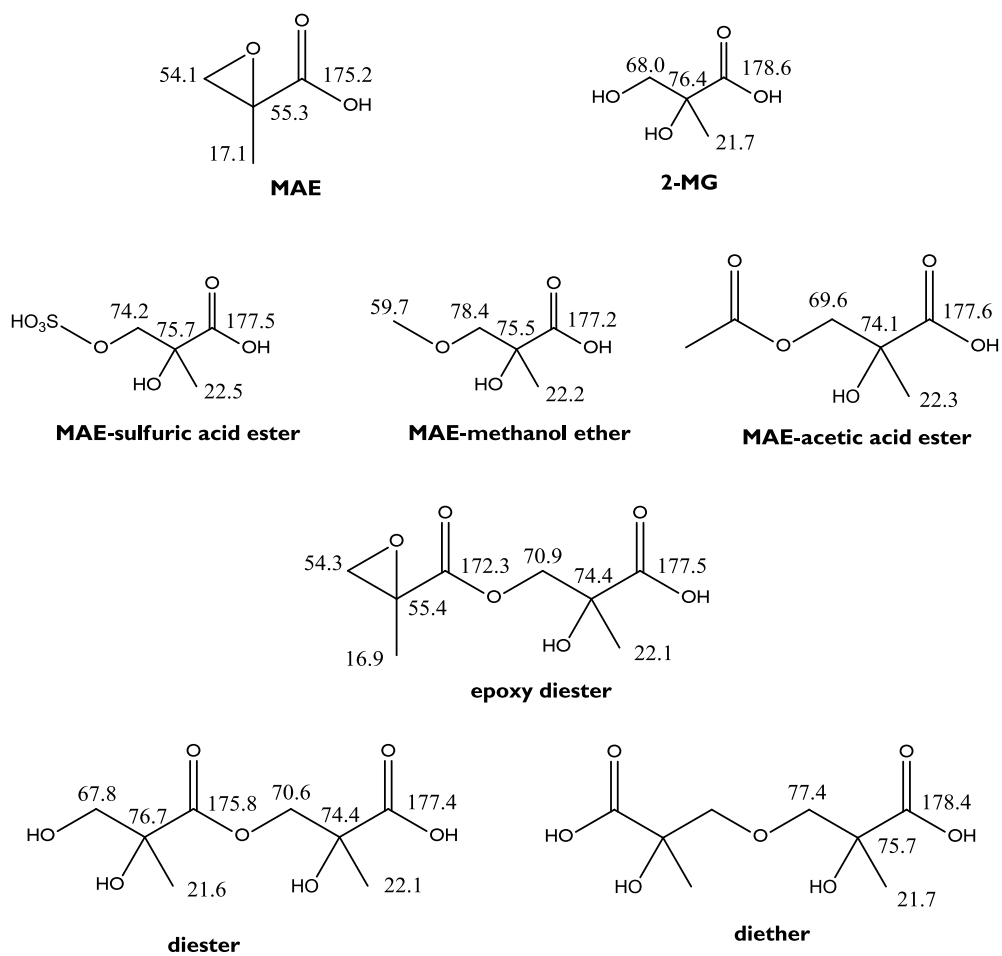
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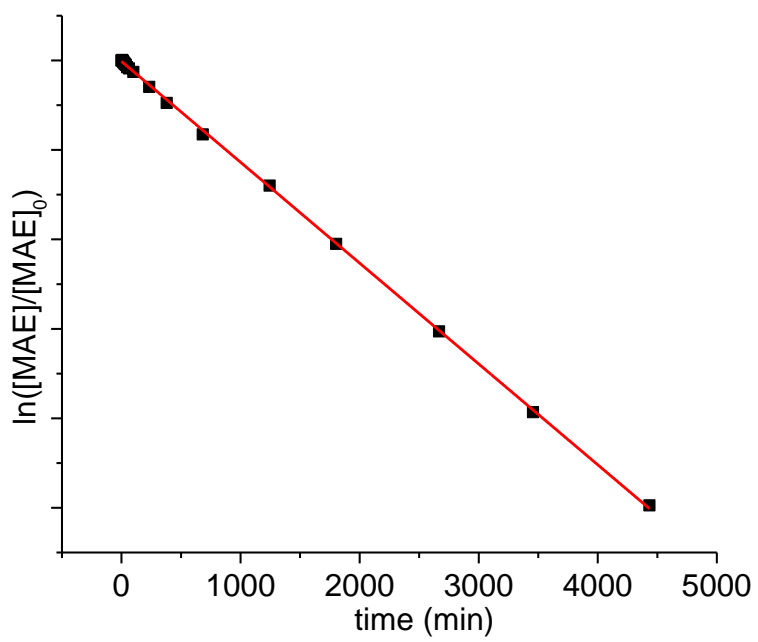
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**Fig. 1.**  $^1\text{H}$  NMR chemical shift assignments for MAE-related species.

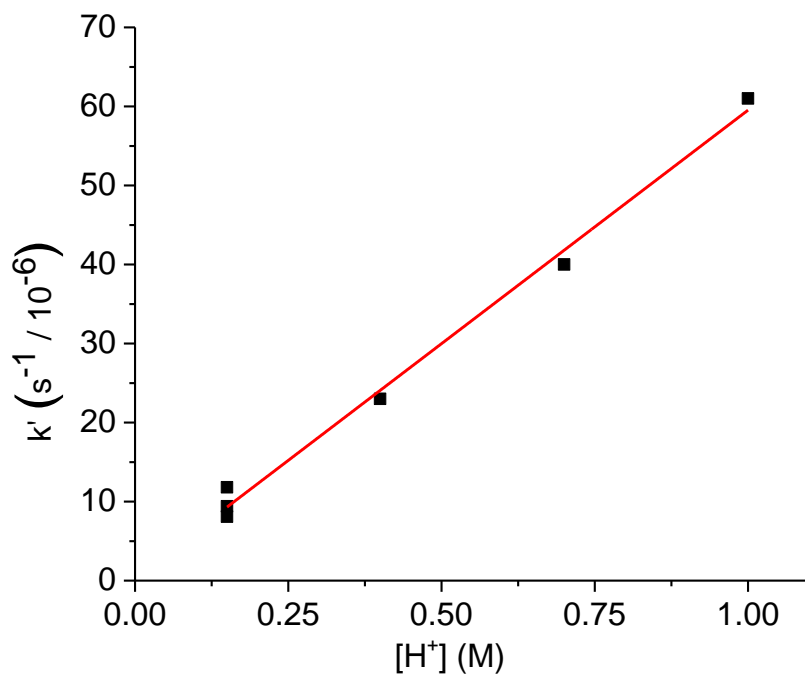


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**Fig. 2.**  $^{13}\text{C}$  NMR chemical shift assignments for MAE-related species.

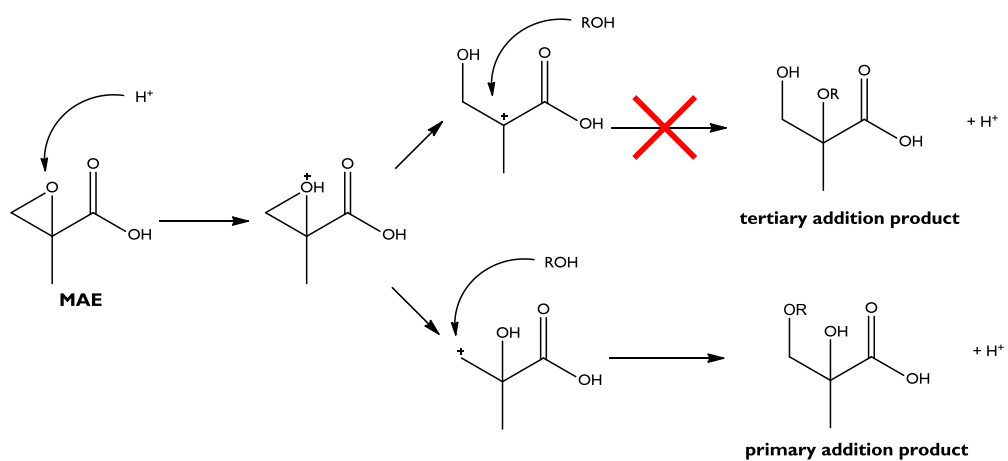


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3 **Fig. 3.** Pseudo first order decay of MAE in 1.0 M D<sub>2</sub>SO<sub>4</sub>.

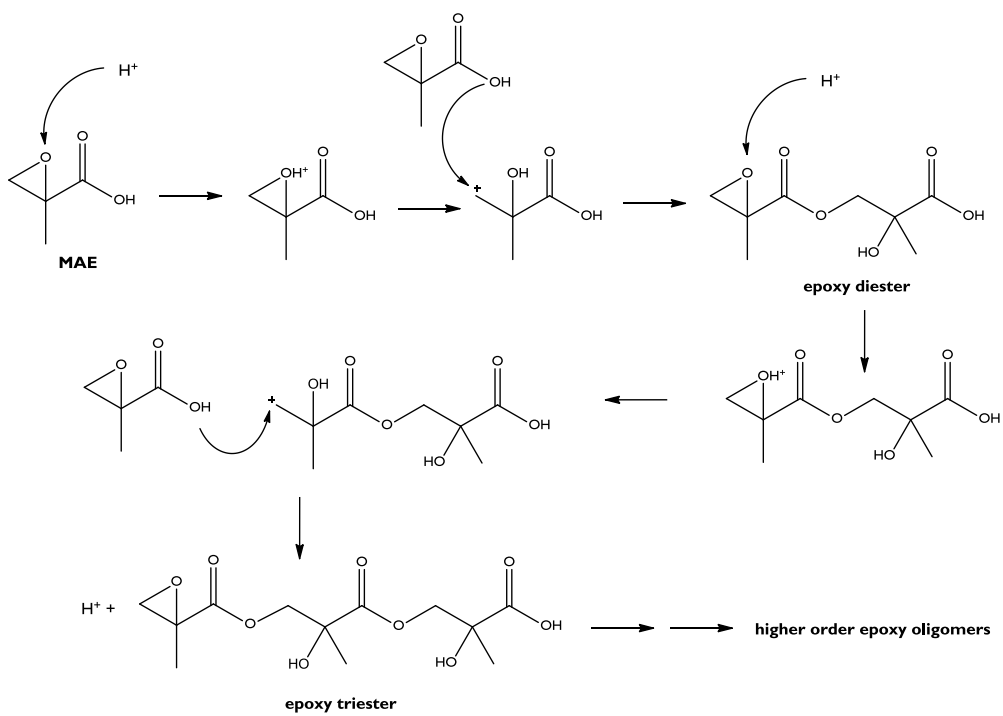


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**Fig. 4.** Determination of acid-catalyzed MAE hydrolysis rate constant.

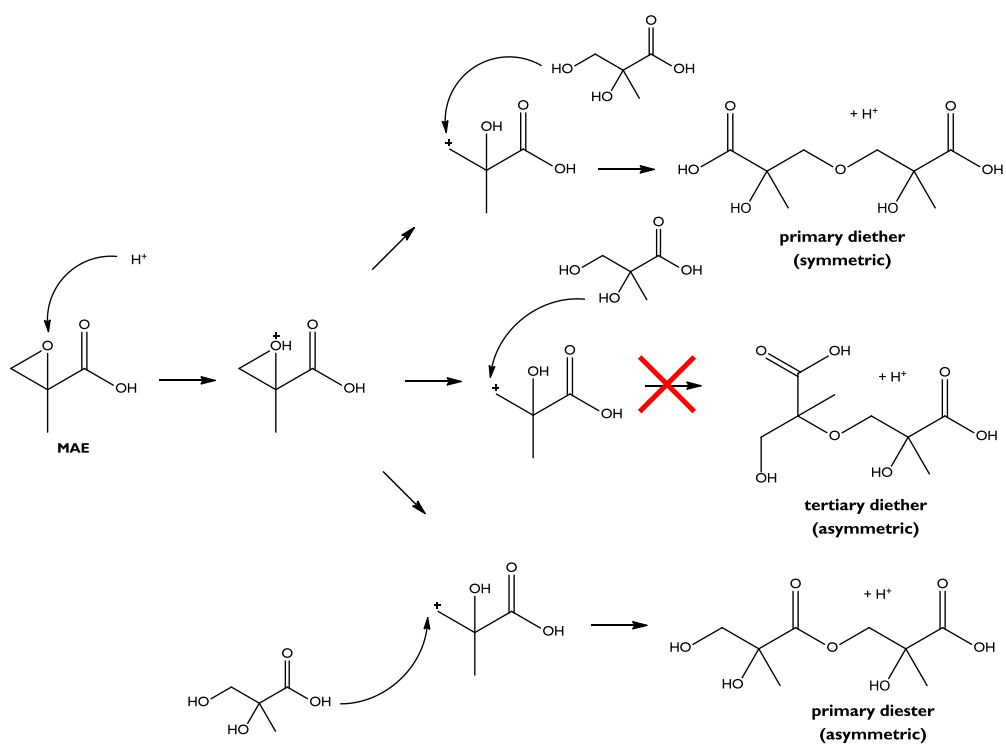


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4 **Fig. 5.** Generalized MAE nucleophilic addition mechanism (the tertiary addition product was  
5 not observed for any MAE + nucleophile reactions).

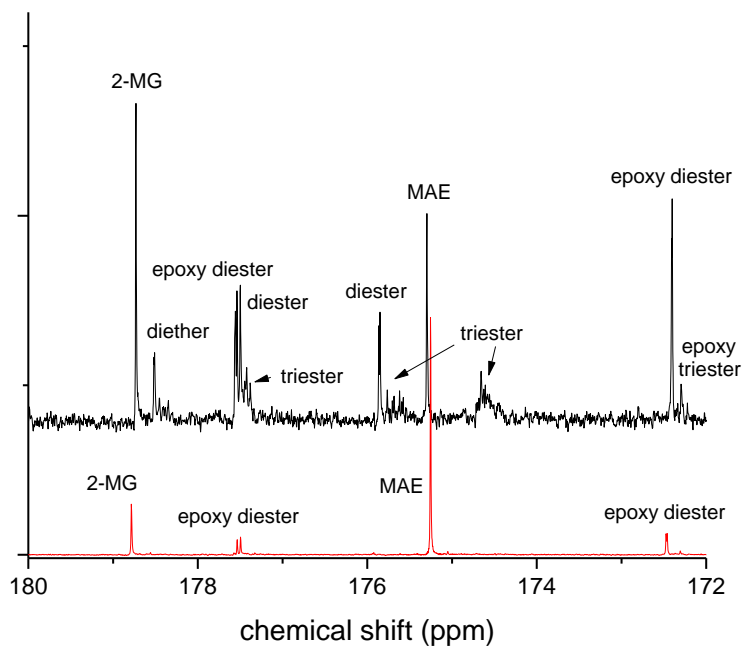


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**Fig. 6.** MAE oligomerization (via epoxy chain reaction) mechanism.

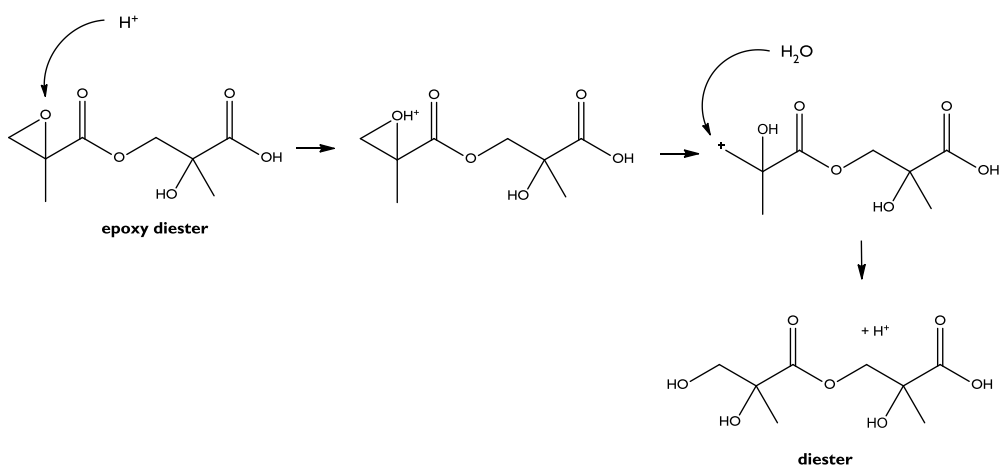


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3 **Fig. 7.** Specific MAE + 2-MG nucleophilic addition mechanisms (the tertiary alcoholic OH  
4 group on 2-MG was not observed to participate in nucleophilic addition reactions).



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 3 **Fig. 8.** Carbonyl region  $^{13}\text{C}$  NMR spectra of early reaction (red trace) and late reaction (black  
 4 trace) ~~neat MAE solutions for experiment #4.~~ See Figure 1 for the molecular species that  
 5 correspond to the NMR peak labels.





- 1
- 2
- 3 **Fig. 9.** Epoxy diester hydrolysis mechanism.