

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 CD₃OD solvent (as opposed to the D₂O solvent used for the other experiments), the chemical shifts differ from the D₂O solvent values given in Tables 1 and 2. While the CD₃OD 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 D₂O 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 D₂O 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 SN₂-like mechanism?

Yes, this is the classic rationale for why SN₂ mechanisms can be favored over SN₁.

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.