

Interactive comment on “Understanding atmospheric peroxyformic acid chemistry: observation, modeling and implication” by H. Liang et al.

Anonymous Referee #1

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The manuscript reports what they claim to be the first atmospheric measurements of peroxyformic acid (PFA) in four field measurements. They also propose that a major source for peroxyformic acid is the reaction of peroxyformyl radicals (HC(O)O_2) with formaldehyde or HO_2 radicals. With the help of a simple box model and many assumptions the authors suggest possible atmospheric implications for their measurements. There are a number of aspects about the manuscript which make me a little uneasy about the authors' claims. The authors are sampling ambient peroxides using a scrubbing coil containing H_3PO_4 in water and analyzing with HPLC after derivatization with a mixture of Hermin and PHPAA. The only justification that the peak they see

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at ~ 8.6 min is PFA appears to be comparison with peaks attributed to PFA in papers from Huang et al. (2013) and Kok et al. (1995). From what they write it would appear that they have not tested the system with an authentic sample of PFA. The authors are reporting quite high pptv mixing ratios for PFA and one wonders how the authors have calibrated the system since apparently PFA is so unstable. Absolutely no information on calibration procedures is given in the manuscript. PFA is an oxidant used widely in chemical processing, synthesis and bleaching. It can be prepared by the acid catalyzed reaction of formic acid (HCOOH) with H_2O_2 and the preparation of aqueous solutions up to 90% are apparently possible but are very unstable. The reaction is reversible and can be increased by increasing the concentration of hydrogen ions. The catalyst can be nitric, phosphoric or sulfuric acid. Although PFA can be produced very readily in aqueous phase there have been no reports in the literature on gas phase reactions leading to formation of PFA. Since solutions of PFA of nearly 90% are possible the low Henry's law constant estimated for PFA by the authors does not seem very credible. FTIR investigations of gas phase $\text{HCHO}/\text{Cl}_2/\text{air}$ systems have failed to produce any evidence for the formation of gas phase PFA the infrared spectrum of which is known (see below). This type of system would involve the PFA formation chemistry which the authors are proposing takes place in the atmosphere, i.e. reactions of peroxyformyl radicals (HC(O)O_2) with HO_2 radicals. Granted Niki et al. (1982) have reported the formation of gas phase PFA in the reaction of O_3 with chloroethylenes, however, the proposed formation mechanism involves reaction of the Criegee intermediate with H_2O and not peroxyformyl radicals. Niki and his coworkers were the first to report the gas phase spectrum of PFA in 1977 thus have experience in handling and detecting PFA. In addition, Niki and coworkers have published several product studies on the reaction of Cl atoms with HCHO in air none of which have reported PFA as a product. If any group was capable of detecting PFA formation in the $\text{Cl} + \text{HCHO}$ system it would have Niki and his coworkers. The lack of observation of PFA in this system makes me very doubtful about the PFA formation mechanism proposed in this manuscript. My doubt is compounded by the known chemistry of HC(O) radicals. The authors propose

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that the peroxyformyl radicals in their mechanism are formed by the reaction of HC(O) radicals with O₂. There have been numerous studies on the reaction of HC(O) with O₂ and using a diverse array of experimental methods, all the experimental evidence supports that the reaction gives CO and HO₂. There have been attempts to measure the peroxyxynitrate HC(O)OONO₂. Photolysis of a HCHO/O₂/Cl₂ system in 1 atm of O₂ at 259 K failed to find any evidence for the formation of HC(O)OONO₂. The only products which could be observed were HOONO₂, HC(O)OH and CO, which indirectly supports that formation of HC(O)O₂ radicals in the reaction of HC(O) with O₂ is of negligible importance. In summary there is no experimental evidence to support the gas phase PFA formation route that the authors are proposing, in my eyes it is simply speculation without any solid experimental foundation. There does not appear to have been any rigorous prior testing of the sampling system for potential artifacts. The authors simply state that PFA is unlikely to be produced in the analytical system since the HCHO precursor for PFA was not added in the eluent and that the H₂O₂ + HCHO reaction in solution does not significantly produce PFA. When sampling in the atmosphere the authors will have HCOOH and H₂O₂ and also acid in their sampling coil all the ingredients necessary for potential formation of PFA. Have the authors tested the analytical technique for the potential in situ formation of PFA in the sampling coil from reaction of HCOOH with H₂O₂? Only after the system has been thoroughly tested for potential measurement artifacts will I believe that the authors are really sampling gas phase PFA. It is also curious that none of the other field measurements of peroxides, many using similar techniques, have not reported signals that could be attributed to PFA particularly since the authors report that PFA correlates well with peroxy acetic acid and the ambient concentrations are reportedly fairly high. Until the detection of gas phase PFA and its gas phase production pathway as speculated by the authors is proven beyond any reasonable doubt there seems little sense in making correlations with other peroxides and in deliberating in detail over possible atmospheric implications as the authors do in the manuscript. The box model they use contains a PFA chemistry scheme which has no basis in experimental fact and uses rate coefficients which

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are simply guessed. It is difficult to take any results produced by such a model very seriously. The peak that the authors detect in their system may well be due to PFA, however, the authors need to prove beyond any reasonable doubt that it is not being produced in their sampling unit. If the peak transpires to be real I suspect the authors will need to look to sources of PFA that potentially include aqueous chemistry of H₂O₂ and HC(O)OH.

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