

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

H. Liang et al.

zmchen@pku.edu.cn

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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 ($\text{HC}(\text{O})\text{O}_2$) 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.

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Thanks for your constructive and thoughtful comments. We have revised our manuscript according to your comments. Below is our response, as shown in answer (A), to your comments.

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 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.

(A): Thanks for your comments and sorry for the confusion. The paper Huang et al. (2013) was a previous study carried out by our group, in which we synthesized a series of organic peroxides including alkyl hydroperoxides, hydroxyalkyl hydroperoxides, and peroxy acids to examine the retention time of different peroxides. In that study, we confirmed that the peak of PFA appeared at 8.6 min in our HPLC system. The instruments we used to measure peroxides in the current study were the same with those used in Huang et al. (2013). Therefore, we have actually tested the system with authentic samples of PFA. We have clarified the manuscript as follows: “In our previous study (Huang et al., 2013), we synthesized a series of organic peroxides including alkyl hydroperoxides, hydroxyalkyl hydroperoxides, and peroxy acids to examine the retention time of these peroxides. In that study, we confirmed that the retention time for PFA chromatographic peak is 8.6 min in our analyzing system (Huang et al., 2013), between the peaks of hydroxymethyl hydroperoxide (HMHP, 7.1 min) and Bis-hydroxymethyl peroxide (BHMP, 8.8 min). The relative position of PFA peak coincides with that reported in Kok et al. (1995).”

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.

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(A): Thanks for the comments. In the current study, authentic samples of PFA were prepared by the acid catalyzed reaction of HC(O)OH with H₂O₂. The acidic potassium permanganate titration method was used to determine the concentration of PFA samples. Using these authentic samples, a multipoint calibration of PFA was done, showing that the PFA resented a good linear response in a wide concentration range relative to the atmosphere. Standard solution of PFA was unstable to reserve, making it difficult to do a direct everyday calibration during the field measurement. Instead, we used the standard solution of H₂O₂ to do single point calibrations for PFA twice a day since response factors for PFA and H₂O₂ were proved to be almost the same in our HPLC analyzing system. We have added the above statements in our 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 H₂O₂ 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.

(A): Thanks for the comments. There have been several reports in the literatures that provided the possibility of gas phase production of PFA. Niki et al. (1982) have reported that the gas phase reactions of O₃ with chloroethylenes can lead to the formation of PFA, which provided the first experimental identification of peroxyformic acid as a product of the gas-phase oxidation of organic compounds. Through they didn't provide direct experimental proof, Osif and Hecklen (1976) proposed that the oxidation of HC(O) radicals in the gas phase can lead to the formation of HC(O)O₂ radicals, which sequentially reacts with HCHO to form 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.

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(A): Thanks for the comments. The 90% PFA solutions was known to be very unstable and was not in equilibrium between the gas and aqueous phase. Therefore, the existence of 90% PFA solution was not helpful to estimate the Henry's law constant. Actually, we found an estimation of the Henry's law constant of PFA in the Hazardous Substances Data Bank (<http://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/6Zu9c3:1> last access: March 21, 2015) using a fragment constant estimation method reported by Meylan and Howard (1991). The estimated value was 1.9×10^{-6} atm m³/mol at 298 K, equivalent to 526 M atm⁻¹, which was on the same order of magnitude with the value we estimated in the current study (210 M atm⁻¹). We have revised our manuscript as follows: "The Henry's law constant of PFA has never been determined in previous experimental studies." and "Therefore, the Henry's law constant of PFA is estimated to be a quarter of the value of PAA, i.e. 210 M atm⁻¹ at 298 K. This value was on the same order of magnitude with that estimated in the Hazardous Substances Data Bank (526 M atm⁻¹ at 298 K, <http://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/6Zu9c3:1> last access: March 21, 2015) using a fragment constant estimation method (Meylan and Howard, 1991)."

FTIR investigations of gas phase HCHO/Cl₂/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)O₂) with HO₂ radicals. Granted Niki et al. (1982) have reported the formation of gas phase PFA in the reaction of O₃ with chloroethylenes, however, the proposed formation mechanism involves reaction of the Criegee intermediate with H₂O 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 Cl + HCHO system it would have Niki and his coworkers. The lack of observation of PFA in this system makes me

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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 are simply guessed. It is difficult to take any results produced by such a model very seriously.

(A): Thanks for your comments and suggestions. Different from chloroethylenes/O₃ system, HCHO/Cl₂/air system is rich of Cl (and perhaps OH) radicals. Once PFA is produced in the HCHO/Cl₂/air system, part of it would be rapidly consumed via Cl/OH radical reactions, thus leading to a low yield of PFA. To the authors' knowledge, FTIR was not able to detect PFA at low level. In order to investigate whether PFA could be produced by HCHO+OH reaction, we have carried out preliminary experiments for gas phase HCHO/O₃/ultraviolet/air system. The results showed that PFA was indeed produced in that system. The detailed description of the experimental procedures and results was added in the supplement materials for the revised manuscript. In addition to our experimental results, some other proofs could also be found in the literatures. Diem and Lee (1982) have reported that the photo-oxidation of formaldehyde in solid oxygen and argon/oxygen matrices at 12 K can yield PFA as a minor product, indicating that HC(O) chemistry can lead to the formation of PFA. Also, Osif and Hecklen (1976) has proposed that the oxidation of HC(O) radicals by O₂ in the gas phase can lead to the formation of HC(O)O₂ radicals, which further reacts with HCHO to form PFA. Therefore, we believed that HC(O) oxidation was able to produce PFA, as we added in the model.

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.

(A): Yes, you are right. We have proved the peak at 8.6 min in our system was due to PFA using authentic samples (Please cf. our answers for the above comments). We have carried out conditional experiments of H₂O₂ and HC(O)OH reaction in the

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aqueous phase, which results proved that PFA can be significantly produced via this reaction only when the concentrations both H₂O₂ and HC(O)OH were above 10⁻³ M. This is because that H₂O₂ and HC(O)OH reaction is reversible and therefore PFA tends to hydrolyze when the water is relatively abundant. We have added these statements in the revised manuscript.

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