Journal: Atmospheric chemistry and physics discussion
Manuscript # : acpd-13-18205-2013
Title: A theoretical model on the formation mechanism and kinetics of highly toxic air pollutants from halogenated formaldehydes reacted with halogen atoms
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After reading the updated version of the manuscript, and the rebuttal of the authors, I remain somewhat disappointed with how the authors dealt with the earlier comments: rather than responding to the criticisms raised, they sidestep many of the issues. I realize that in some cases this might be caused by a language problem, but several things really need to be addressed in the paper to avoid confusing or misleading the audience. I would therefore like to raise some of these issues again, with a more detailed indication of why I feel a proper response is necessary.

All of the issues raised can be easily resolved by properly stating that the level of theory selected fortuitously gives the correct answer, by replacing the incorrect secondary chemistry, and by openly discussing some computational aspects of the work. Because the authors chose to avoid a proper revision of the manuscript, I can no longer support publication of this manuscript until appropriate corrections are made.

Section 1) Incorrect attribution of text to the referee

Question 11: "*review: ... these are connected to free energy, not to energy. The Authors have certainly free energy estimates available, they could use them."*
Answer: "As for free energy estimation, we think the reviewer might confuse "the free energy" with "the activation energy". It is because for atmospheric reactions, the activation energy is more trustable than the free energy. Thus, in...."

These sentences were NOT in my review. Please refrain from adding text to the review, and then admonishing the referee on your own additions.

Section 2) Relevance of the work, and the chemical pathways presented.

Question 2, Question 4, and Question 11 repeatedly ask the authors to examine their reaction system with regard to the concentrations of halogens in the atmosphere, i.e. they are asked to show the relevance of their work.
Despite these questions, and their direct impact on the relevance of the paper, the authors still do not list any concentrations of halogens in the atmosphere, nor do they acknowledge that these concentrations (with the possible exception of chlorine atoms) are probably too low to allow halogen atoms to be a significant sink of the formaldehydes studied, compared to other oxidants such as OH. They repeatedly claim or imply that the fluorine-driven chemistry is the main atmospheric degradation process, when F-atoms have likely a negligible concentrations anywhere in the atmosphere. As such, they overstate the importance of their findings, and furthermore confuse the audience as to which reactions might be worthwhile to include in an atmospheric model. Changing wording of "high concentration" to "abundant" (response to question 4) does not constitute a response to these questions, nor does a rebuttal that the authors really refer to the higher *rate coefficient* of the fluorine reactions.

Question 12, Question 13, and Question 14 relate to the subsequent chemistry of the predicted products.

In the first version, the authors presented secondary chemistry in a way that made it appear as if they did calculations on the proposed reactions. In this revised version and rebuttal, the authors now state that they did not do calculations on several of the reactions, and rather rely on earlier work by Hewitt et al. and Edney et al. Please note that in a scientific publication all sources must be properly acknowledged even at the first submission, and no external data is to be presented in such a way that it appears to originate from the authors. Otherwise, the authors open themselves to suspicion of plagiarism.

Regarding the fate of trans-ClC(O)OO : The authors now cite Hewitt et al, 1996, claiming that trans-ClC(O)OO will undergo a concerted decomposition to CO2 + ClO. Nothing in the paper of Hewitt et al. suggests that this reaction will occur: their source of CO2 is crossreaction of the acylperoxy radicals ClCO3+ClCO3, forming two acyloxyradicals that decompose to CO2. Furthermore, Hewitt et al don't differentiate between cis- and trans-ClC(O)OO, so the distinction the current authors make with cis-ClC(O)OO appears arbitrary.

One of the review comments also indicated that, in the atmosphere, it is highly unlikely that ClC(O)OO will cross-react, as the ClC(O)OO concentration will be too small compared to other co-reactants of RO2 molecules, such as NO, HO2, CH3OO, CH3C(O)OO, and other RO2 radicals. The authors sidestep this, claiming that "*the pathway from bis-(cis-ClCO3) should not in line [sic] with RO_2+RO_2 reaction because three O atoms existed in this species. That is, the electronegativity on R group between the case of two and three O atoms are different.*". Apparently, the authors are unaware of the existence of acetylperoxy radicals, CH3C(O)OO, of importance in the atmosphere in e.g. the formation of PAN. They also choose to ignore the HO2 reaction, which is mentioned in the literature they cite, and apparently also didn't read the following quote from Hewitt et al. 1996: "*We expect that ClC(O)O2 also reacts with ClO2, HO2, CH3O2, and the other peroxy radicals in the cell, in a similar manner to the reactions of CH3O2, CH3C(O)O2, and CCl3O2.*". The authors also refer to Endey et al., 1992, but this has no bearing on the atmospheric fate of the ClC(O)OO radicals, as that study is experimental labwork with much higher concentrations of these radicals compared to the atmosphere, and with no other competitive coreactants available.

Finally, in the paper the authors claim formation of Cl2 from the cross-reaction of ClC(O)OO+ClC(O)OO. Cl2 as a direct product is in strong disagreement with well-established reactions of acylperoxy radicals. See Hewitt et al. for a correct representation of the chemistry (reaction 4 and 6). In the rebuttal, the authors now claim recombination of Cl atoms as the source of Cl2, but fail to make this clear in the paper. I propose that, unless the authors actually discuss a more complete Cl-atom chemistry in the atmosphere, the authors should present the Cl atom as the reaction product.

Section 3) Methodological problems in the quantum chemical calculations

Question 5: Scaling of MP2 frequencies and ZPE.

The authors use MP2 frequencies and ZPE unscaled. This is not a correct methodology, and biases the authors predictions. The recommended scaling factor for MP2/6-311G(d,p) frequencies is 0.970 for ZPE and 0.984 for vibrational frequencies (Database of Frequency Scale Factors for Electronic Model Chemistries, maintained by J. Zheng, I. M. Alecu, B. J. Lynch, Y. Zhao, and D. G. Truhlar). This will affect the predicted rate coefficients. The authors do not list ZPE corrections separately, but I roughly estimate a 20% impact on k(298K).

Question 19: "Supplement, page 1: It would have been useful to perform higher-level calculations on the smallest system to verify the accuracy of the predictions. It appears the current results rely somewhat on cancellation of error. Note that the differences of 0.5 kcal/mol already imply an uncertainty of over a factor of two on the predicted rate coefficient. The main manuscript does not present any error analysis on the predictions, other than to note that they (perhaps fortuitously) match the available experimental data.
Response: It is not accidental that PMP2//MP2 level was performed to calculated our reaction systems, and the comparison of methods was also carried out, not only between high and low levels but also Ab Initio and DFT methods (in Supplement). Therefore, the results of "our calculated results match the available experimental data" are not fortuitously obtained."

The authors strongly overstate the intrinsic reliability of their methodology, and fail to realize that they merely have selected a method that provides apparently correct answers based on cancellation of error. The intrinsic reliability of MP2 and PMP2 is a few kcal/mol, at best. For the current reactions, it just happens to give mostly correct values. Considering that the authors do not even apply the methodology properly (e.g. no scaling of ZPE and frequencies, no PMP2 geometry optimizations, no IRC-Max calculations,...) it is nothing short of fortuitous that they get good results. I state here clearly that this paper would have been rejected out of hand due to the low level of methodology if there had not been experimental reference data.

Question 19 continued response : "Considering spin contamination in HF wavefunctions, the PMP2 method was selected to reduce some errors in calculated vibrational frequencies at MP2 level in this study."

The paper states PMP2//MP2 as the level of theory: this means PMP2 single point energies on an MP2 geometry and MP2 vibrational frequencies. Table S2 and S3 list frequencies (strictly speaking "wavenumbers") calculated at the MP2 level of theory. I could not find a single instance of PMP2-based vibrational analyses. Selecting PMP2 for the single point energies does NOT correct errors on the vibrational frequencies. The fact that the authors indicate errors in the calculated MP2 frequencies suggests further problems with their selected level of theory. In Question 20, the authors again erroneously claim that a spin-projected level of theory for single point energies implies a negligible influence of spin-contamination on the geometry optimization and the frequency analysis.

Question 19 continued response : "For clarity, another section was also modified as "The computational results indicated that compared with the values of high-accurate QCISD(T)//MP4 level, the values of PMP2//MP2 level within the error limit of 0.21 kcal/mol are more closer than that of MP2//MP2 level with the error limit of 1.77 kcal/mol. Therefore, MP2//MP2 level was discarded without discussion in main text" Please see p. 2 line 3-6 in the revised Supplement."

Again the authors strongly overstate the reliability of their methodology. Table S1 indicates differences of over 1 kcal/mol between the PMP2//MP2 and QCISD(T)//MP2 level of theory, which implies uncertainties of over a factor of 5 at room temperature based on their geometries. The difference between QCISD(T)//MP2 and QCISD(T)//MP4 is listed at 0.7 kcal/mol, with an associated factor of 3 uncertainty in predicted rate coefficient. Hand-picking the comparison between PMP2//MP2 against QCISD(T)//MP4 as less than 0.21 kcal/mol (for only two reference compounds) does not imply a reliable method, only a possibility of cancellation of error.

Section 4) methodological problems in the kinetic calculations

Question 8, "*p. 18213 line 22: "...indicating a *kinetic* competition..." It is unclear how this indicates a kinetic competition. All things being equal, a difference in barrier height of 4 kcal/mol implies a rate constant difference of about 3 orders of magnitude at atmospheric temperatures. Nor is it clear to this referee what the difference with "thermo dynamical competition" is.*

*Response: We do not think your deduction is right. That is, a difference in barrier height of 4 kcal/mol may not imply a rate constant difference of about 3 orders of magnitude at atmospheric temperatures. It is because that according to the calculated equation of the rate constants k(T,s) = (alpha/h*beta)*[Qgt(T,s)/Qr(T)]*exp[-beta*Vmep(s)], the rate constant depend on not only reaction temperature but also VMEP(s), in which VMEP(s) is the classical energy along the minimum-energy path (MEP) and is constructed to depend on the potential barrier energy and reaction energy. Thus, the rate constants were decided not only by the potential barrier energies but also by the reaction energies as well as the reaction temperatures. Therefore, the accurate rate constant and branching ratio should not be determined only from the mechanism aspect but also from the kinetic aspect. In the mechanism section, the kinetics competition was discussed from the point view of the potential barrier energy, while the thermodynamics competition was discussed from the point view of the reaction energy. For example, although the potential barrier energy of F-addition pathway was higher than that of the corresponding H-abstraction pathway by 4 kcal/mol−1, two pathways should be a kinetic competition if the exothermic energy of F-addition pathway is enough to overcome the potential barrier energy of 4 kcal/mol−1.*"

A change in Vmep(s) of 4 kcal mol-1 in the above formula induces a change in the rate constant of about 3 orders of magnitude at room temperature. The deduction is mathematically correct, and is neither new nor surprising. The authors can not state that a similar reaction with a barrier 4 kcal mol-1 higher than another reaction can be competitive at room temperature, as that is simply not correct. This could only happen if the reactions compared are significantly different entropically, which is certainly not the case here. Also, a reaction rate does not depend on the reaction exothermicity as the products are nowhere included in the rate expression. Only the reactants, and the barrier shape, height, and characteristics of the degrees of freedom along that MEP are relevant (see equation above). No matter how large the "exothermic energy of F-addition" is, that energy simply does not influence the rate calculations. I suspect the authors are referring to the Evans-Polanyi relationship, which is not relevant for the problem discussed.

I will ignore the kinetic versus thermodynamic competition section as this is probably a translation issue. Kinetics is governed by thermodynamics, and I can't see how they can be separated. I suspect the authors want to discuss energetic (i.e. barrier height) versus entropic (i.e. TS rigidity) effects that affect the kinetics in different ways, but the authors' arguments don't match one-to-one to these concepts.

Question 16: p. 18218 line 23: "the rate constants decreased with increasing altitudes". This indicates a positive temperature dependence, while many barrierless reactions show a negative temperature dependence. This might be worthwhile to discuss.

Response: The reactions of the halogenated formaldehydes with halogen atoms were not barrierless processes. For clarity, this sentence was revised as "the rate constants of halogenated formaldehydes reaction with halogen atoms decreased with the increase of the altitudes". Please see p. 18218 line 23.

On page 18210 and 18211, the authors present several negative delta-E values. Also, on page 1821 they state that "*For F-Rabs-Cl, Cl-Rabs-Cl, F-Rabs-Br, Cl-Rabs-Br, and Br-Rabs-Br pathways, the energy barrier heights were positive without the ZPE corrections, while it became negative via the ZPE correction (Table 1).*", implying furthermore that the reactions mentioned just before (Cl-Rabs-Cl and Cl-Rabs-Br) had negative barrier even prior to ZPE correction. Table 1 lists mostly negative barrier heights, which the caption calls “potential barrier heights”, (i.e. potential energy prior to ZPE-corrections; if they are not potential energy barriers, it should have been mentioned that they are ZPE-corrected). Finally, the authors use variational TST theory, designed to deal with barrierless or near-barrierless reactions. In view of all that, claiming in the rebuttal that the reactions are not barrierless is confusing, if not outright in disagreement with the paper. I restate that this aspect needs to be discussed properly, discussing the influence of a submerged barrier (and the pre-reactive complex that this implies), and discussing the temperature dependence of such reactions.

Section 5) other remarks

Question 10: p. 18215 line 22: missing units of K in the exponential function. Also in other Arrhenius expressions.

Response: According to the reviewer’s comment, the units of K were added as “0.99×10−11 exp[−813/T(K)]” in the corresponding place of Arrhenius expressions.

The correct way to write this is exp(-813K/T).

Question 17: p. 18227 table 3: indicate units of C

Response: According to the reviewer’s comment, unit of C was indicated as “C =E / R , E = Ea − nRT, R is the gas constant (Zheng et al., 2010).”

The units of C used in table 3 are Kelvin. What the authors added is equations on how to calculate it, which is not what was asked, as that also depends on the units used in those formulas. Please always indicate physical values and parameters as numbers with units (if they have any); different fields of research have different default expectations of units.