Atmos. Chem. Phys. Discuss., 13, C4754–C4758, 2013
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Atmospheric Chemistry and Physics
Discussions
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Interactive comment on "A theoretical model on the formation mechanism and kinetics of highly toxic air pollutants from halogenated formaldehydes reacted with halogen atoms" *by* Y. M. Ji et al.

Anonymous Referee #1

Received and published: 12 July 2013

This manuscript describes a very thorough theoretical study of the reaction of halogen atoms with halogenated formaldehydes. The level of quantum chemical theory used is rather low, being based on MP2 only, where the level of theoretical kinetic methodology is more in line with the state of the art. Still, the final predictions agree favorably with the available experimental data, indicating that for the title reactions the level of theory is sufficient. As such, the complete set of predictions, including those for which no experimental data is available for comparison, can be considered sufficiently reliable.

In addition to the characterization of the direct reaction kinetics, the authors assess the continued atmospheric degradation of the reaction products. While there is nothing wrong with this analysis as such, it might have been more useful for the target audience to focus this analysis on the most relevant atmospheric processes. Examples of this include the proposal that ClCO radical would primarily react with Cl atoms “for high atmospheric concentrations of Cl atoms”, when a barrierless reaction with O2 seems a much more likely prospect considering the relative concentrations of Cl versus O2 anywhere in the atmosphere. Another example is the reaction of halogenated acylperoxy radicals with twin acylperoxy radicals, where in general the reactions with generic HO2/RO2/NO seems statistically the most likely channels, and hence what atmospheric scientist would like to put in their chemical models. The atmospheric fate is furthermore discussed without accounting for the relative concentration of the co-reactant concentrations. The article thus falls short of determining the atmospheric fate.

Regardless of the above minor criticism, and the small comments below, I recommend this paper for publication.

Other comments:

Abstract, p. 18206 line 15: “Reactions with F atoms occurred more easily than those with Cl and Br atoms”. This phrasing implies that reactions with F-atoms are the dominant channel; however, this depends on the relative concentration of F-atoms compared to Cl and Br in the atmosphere.

p. 18206 line 17: “Arrhenius formulas” -> Arrhenius equations.

p. 18207 line 10: “high concentrations of these halogen species”. Give an indication what concentration levels are discussed.

p. 18208, method. Scaling of the MP2 frequencies and ZPE is never mentioned, but must be indicated.

p. 18212 line 17 and line 19. The number of significant digits on the calculated enthalpies far exceeds their reliability.

p. 18213 line 16: “...as the molecular weight of the halogen atom was increased”. It is likely not the weight, but the electronegativity of the atom that makes the difference.

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 “thermodynamical competition” is.

p. 18214 line 16: “the lone pair of electrons on the C atom of the carbonyl group”. The C-atom and the H-atom are the only two atoms in the molecules studied that do not have a lone pair. Do the authors mean the pi-bond with the oxygen, or perhaps the p-orbital involved in said pi-bond ?

p. 18215 line 8, line 15 : The number of significant digits on the calculated rate constants far exceeds their reliability.

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

p. 18216 line 15: “results showed that the reactions of F-atoms with haloformaldehydes were more important in the degradation process”. This has not been shown. It has only be shown that the reactions are faster, but the relative concentration of the halogen atoms needs to be accounted for before the dominant degradation process can be determined. This has not been addressed anywhere in the manuscript, nor the competition against traditional oxidants such as the OH radical. Hence, it is as yet unestablished what the contribution of the studied reactions is in the actual atmospheric chemistry.

p. 18217 line 24: “for trans-ClCO3, the most feasible pathway was to undergo a con-

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certed O-shift and C-Cl bond cleavage.” I could not find any computational results on this, nor an estimate of the barrier height or rate coefficient.

p. 182147 line 25: “Two cis-ClCO3 could easily combine with each other”. True, but it is not established that this is competitive against the traditional RO2/HO2/NO reactions, or the isomerisation to trans-ClCO2 and subsequent unimolecular decomposition.

p. 18217 line 28 “CCl(O)OOCCl(O) could further decompose to produce CO2 and Cl2”. I could not find any computational results on this. Formation of Cl2 seems unlikely.

p. 18218 line 4: “HC1” typo “one” should be “ell”.

p. 18218 line 6: “high atmospheric concentration of Cl atoms”. Define “high”.

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.

p. 18227 table 3: indicate units of C

p. 18229 figure 2: indicate in the caption what the different panels a-f indicate. As it stands, the figure can not be interpreted without the text.

p. 18230 figure 3: If the H-shift and Cl-C bond cleavage is concerted, it is unclear why multiple arrows are shown for trans-ClC(O)OO -> CO2 + ClO. The path from bis-(cis-ClCO3) to CO2 + Cl2 is unclear, and not in line with traditional RO2+RO2 chemistry.

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.

Supplement, page 1. MP2 often suffers from spin contamination, but this is not discussed anywhere.

Supplement, page 2: “t” for the TS partition function should be capital T (temperature)

Supplement, page 13, table S2: indicate units.

Supplement, page 19, table S8: indicate units.

Supplement, page 21, table S10: Wikipedia might not be the most appropriate reference, when original literature sources are available for these data.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 18205, 2013.