Reply to "Comment on 'Atmospheric Chemistry of Linear Perfluorinated Aldehydes: Dissociation Kinetics of $C_nF_{2n+1}CO$ Radicals'"

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Received: July 6, 2007; In Final Form: October 30, 2007

We thank Wallington et al. for their careful reading of our recently published ab initio study of the decomposition of $C_nF_{2n+1}CO$ radicals.[1] In our study, we showed that $C_nF_{2n+1}CO$ radicals have a strong tendency to decompose to give C_nF_{2n+1} and CO under atmospheric conditions. These results are in sharp contrast to the available experimental data for linear $C_nH_{2n+1}CO$ radicals, which nearly exclusively add O_2 to form acyl peroxy radicals.[2] As noted by Wallington et al., the results we reported are entirely consistent with recent laboratory[3,4] studies indicating that decomposition via CO elimination (reaction 1) is an important atmospheric fate of $C_nF_{2n+1}CO$ radicals

$$C_nF_{2n+1}CO \rightarrow C_nF_{2n+1} + CO \tag{1}$$

In their comment, Wallington et al. do not dispute the main thrust of our paper but instead focus on a statement we made within the Introduction and Conclusion sections of our paper which is said to be "....inconsistent with the literature data and worthy of comment."

Specifically, Wallington et al. object to part of our discussion of the consequences of incorporating radical decomposition via reaction 1 directly into the Ellis et al.[5] pathway to PFCAs. As we discussed in our paper, Hurley et al.[4] increased the PFCA yields found in their earlier work to account for the fraction of $C_nF_{2n+1}CO$ that decomposes. For example, the yield of $C_4F_9C(O)OH$ from the reaction of C_4F_9CHO with Cl atoms in the presence of HO_2 was previously reported[6] as 8 ± 2%. Since the yield of $C_4F_9C(O)O_2$ radicals measured by Hurley et al.[4] was 11%, the adjusted yield of $C_4F_9C(O)OH$ is $0.08/0.11 = 73\%$. As we said in our paper, this reasonable procedure leads to yields that are hard to reconcile with the literature. In addition, we noted that the adjusted yields of $C_nF_{2n+1}C(O)OH$ from the reaction of $C_nF_{2n+1}CHO$ with Cl atoms show a strongly increasing trend; the yields are 39 ± 4, 50 ± 8, 53 ± 11, and $73 \pm 18\%$ for $n = 1-4$, respectively, which runs counter to the notion of the diminishing role of the lengthening perfluoroalkyl chain evidenced in our calculated activation energies.

We further noted that there is no support in the limited available literature for yields in excess of 70% in the reactions of acyl or fluoroacyl peroxy radicals with HO_2, and in addition, the available literature indicates that the corresponding reaction of R_FO_2 radicals with HO_2 to give R_FOH does not occur. It seems particularly telling that CF_3CHFO_2 reacts with HO_2 to give the peroxide $CF_3CHFOOH$ and O_2 in unit yield.[7] Finally, we suggested that one or more additional pathways to PFNA is missing from the Ellis et al.[5] scheme and provided an example of such a pathway in the work of Tuazon and Atkinson.[8]

All of this part of our analysis is unchallenged in the Wallington et al. comment. Instead, they chose to focus on our claim that "this ingenious mechanism is essentially unsupported in the literature". The mechanism in question was proposed by Ellis et al.[5] and begins with the reaction of $C_nF_{2n+1}O_2$ and an α-dihydrogenated peroxy radical RH_2O_2 to give an unstable α-fluoro alcohol

$$C_nF_{2n+1}O_2 + RH_2O_2 \rightarrow C_nF_{2n+1}OH + RHO + O_2 \tag{2}$$

It is this step that we believe is "essentially unsupported". As Wallington et al. point out, the corresponding disproportionation reaction occurs readily for many nonfluorinated alkyl peroxy radicals. The question is, do perfluorinated peroxy radicals also disproportionate via reaction 2? As we stated in our paper, to the best of our knowledge, there have been no experiments in which a fluorinated peroxy radical reacts with an α-dihydrogenated peroxy radical. Wallington et al. do not dispute this statement.

One might argue that the existing literature for nonfluorinated alkyl peroxy radicals suggests that reaction 2 should proceed with reasonable yield, but if we have learned anything from the recent work on decarbonylation of $C_nF_{2n+1}CO$ radicals, it is that we should be very wary of inferring the properties of fluorinated radicals from those of hydrocarbon radicals. It is difficult to draw any strong conclusions, given the very limited existing experimental data on fluorinated analogues. It was in this light that we included a discussion of the self-reaction of α-hydrogenated fluoroperoxy radicals. As we stated in our paper, the available literature shows that the disproportionation self-reaction of α-hydrogenated fluoroperoxy radicals "has, at best, a very small yield". There is nothing in the comment of Wallington et al. that disputes this statement; indeed, the authors confirm our statement. Wallington et al. say that in their studies of the self-reaction of CH_2FO_2[9] and CHF_2O_2,[10] they "did not conclude that the alcohol yield in these reactions was 'zero'". An examination of the first of these papers[9] shows that neither CH_2FOH nor its expected decomposition HCHO were detected in the self-reaction of CH_2FO_2, the combined yield of HC(O)F and CH_2FOOH is 98 ± 10%, and the authors concluded that the self-reaction of CH_2FO_2 "proceeds predominantly, if not exclusively, by" a radical pathway. Likewise, in their paper on the self-reaction of CHF_2O_2,[10] no CHF_2OH was detected in the chamber, and the authors write that the self-reaction of CHF_2O_2 "proceeds predominantly, if not exclusively, via" a radical pathway. As we noted in our paper, the preferred value of the CH_2FOH yield in the self-reaction of CH_2FO_2 is reported as zero in the latest *Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry* provided by IUPAC.[7]

In the foregoing, it may seem that we have significant disagreements with Wallington et al. on the atmospheric fate of $C_nF_{2n+1}CO$ radicals, but that is not the case. Both groups agree that $C_nF_{2n+1}CO$ radicals have a strong tendency to decompose to give C_nF_{2n+1} and CO under atmospheric conditions, neither contends that 100% of the radicals decompose, and the bulk of our analysis of the consequences of radical decomposition is not disputed by Wallington et al. The few areas in which we disagree can be resolved by additional experimental studies. In particular, additional chamber experiments could be performed in which methane is added in varying amounts to the chamber. If the mechanisms proposed in Ellis et al.[5] and reiterated in the comment of Wallington et al. are correct, the production of lower PFCAs should rise monotonically with

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10.1021/jp075291d CCC: $40.75 © 2008 American Chemical Society
Published on Web 12/28/2007

increasing methane mixing ratio. It would be most helpful if Wallington et al., or another group with similar facilities, were to perform such experiments.

References and Notes

(1) Waterland, R. L.; Dobbs, K. D. *J. Phys. Chem. A* **2007**, *111*, 2555.

(2) Jagiella, S.; Libuda, H. G.; Zabel, F. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1175.

(3) Solignac, G.; Mellouki, A.; Le Bras, G.; Barnes, I.; Benter, T. *J. Phys. Chem. A* **2006**, *110*, 4450.

(4) Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Andersen, M. P. S.; Nielsen, O. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. *J. Phys. Chem. A* **2006**, *110*, 12443.

(5) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. *Environ. Sci. Technol.* **2004**, *38*, 3316.

(6) Andersen, M. P. S.; Stenby, C.; Nielsen, O. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Martin, J. W.; Ellis, D. A.; Mabury, S. A. *J. Phys. Chem. A* **2004**, *108*, 6325.

(7) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F. J.; Hynes, R. G.; Jenkin, M. E.; Kerr, J. A.; Rossi, M. J.; Troe, J. *Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry*; IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry: Research Triangle Park, NC, 2006.

(8) Tuazon, E. C.; Atkinson, R. *Environ. Sci. Technol.* **1994**, *28*, 2306.

(9) Wallington, T. J.; Ball, J. C.; Nielsen, O. J.; Bartkiewicz, E. *J. Phys. Chem.* **1992**, *96*, 1241.

(10) Nielsen, O. J.; Ellermann, T.; Bartkiewicz, E.; Wallington, T. J.; Hurley, M. D. *Chem. Phys. Lett.* **1992**, *192*, 82.