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COMMENTS

Comment on “Atmospheric Chemistry of Linear Perfluorinated Aldehydes: Dissociation Kinetics of $C_nF_{2n+1}CO$ Radicals”

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Waterland and Dobbs[1] reported the results of a quantum mechanical study of the decomposition of $C_nF_{2n+1}CO$ radicals. Their results are consistent with recent laboratory[2,3] and theoretical[4] studies indicating that decomposition via CO elimination can be an important atmospheric fate of C_nF_{2n+1}-CO radicals (particularly for the longer members of the series). In the discussion of the environmental context and ramifications of their results, Waterland and Dobbs make a claim which, in our opinion, is inconsistent with the literature data and worthy of comment.

The claim (made on page 2560[1]) is “this ingenious mechanism is essentially unsupported in the literature”. The mechanism in question is the simplest explanation of the observed formation of a series of perfluorocarboxylic acids during the simulated atmospheric oxidation of long-chain fluorinated alcohols[5] and consists of three steps

$$C_nF_{2n+1}O_2 + CH_3O_2 \rightarrow C_nF_{2n+1}OH + HCHO + O_2 \quad (1)$$

$$C_nF_{2n+1}OH \rightarrow C_{n-1}F_{2n-1}C(O)F + HF \quad (2)$$

$$C_{n-1}F_{2n-1}C(O)F + H_2O \rightarrow C_{n-1}F_{2n-1}C(O)OH + HF \quad (3)$$

Reaction 1 is the disproportionation channel in the reaction between CH_3O_2 and a perfluoroalkyl peroxy radical. It was established 50 years ago by Russell[6] that the disproportionation channel is important in the reaction between peroxy radicals in which at least one of the peroxy radicals contains an α-hydrogen atom. There are numerous reactions between peroxy radical reactions (e.g., $CH_3O_2 + CH_3O_2$, $C_2H_5O_2 + C_2H_5O_2$, i-$C_3H_7O_2$ + i-$C_3H_7O_2$, and $CH_2ClCH_2O_2 + CH_2ClCH_2O_2$[7]) in which it has been established that the disproportionation channel is important.

Waterland and Dobbs support their claim by citing product yields in the self-reaction of CH_2FO_2, CHF_2O_2, CF_3CFHO_2, and $CHF_2CF_2O_2$ radicals. In studies of the products of the CF_3-$CFHO_2$ radical self-reaction, extrapolation of the $CF_3C(O)F$ yield to zero [O_2] gave a molar $CF_3C(O)F$ yield and, by inference, a molar CF_3CHFOH yield of approximately 0.049−0.08 at 298 K, with some evidence of higher yields at lower temperature.[8,9] The self-reaction of CF_3CFHO_2 radicals proceeds via a small, but significant, disproportionation channel. $CHF_2CF_2O_2$ radicals do not possess an α-hydrogen atom and will not undergo disproportionation. In studies of the products formed following the self-reaction of CH_2FO_2[10] and CHF_2O_2[11] radicals, we concluded that the self-reactions proceed predominately via radical-forming channels. We did not exclude the possible existence of a minor (≤10%) disproportionation channel. Contrary to the statement by Waterland and Dobbs,[1] we did not conclude that the alcohol yield in these reactions was “zero”. The proposed reaction 1 is supported by the literature data.

Heterogeneous decomposition of α-halogenated alcohols such as CF_3OH,[12,13] CH_2ClOH,[14] $CHCl_2OH$,[14] CCl_3OH,[14] and $CH_3CHClOH$[15] via elimination of HF or HCl has been shown to be an important loss mechanism for these alcohols in smog chamber experiments. Theoretical work also points to the importance of heterogeneous decomposition as an atmospheric fate of CF_3OH.[16] The proposed reaction 2 is supported by the literature data.

The perfluoroacylfluoride $C_{n-1}F_{2n-1}C(O)F$ is unreactive with respect to gas-phase atmospheric chemistry and will not be photolyzed by the sunlight available in the troposphere.[17] There is little doubt that the atmospheric fate of $C_{n-1}F_{2n-1}C(O)F$ is hydrolysis upon contact with cloud-rain seawater or atmospheric aerosols.[17] The proposed reaction 3 is supported by the literature data.

To conclude, reactions 1−3 provide the simplest explanation of the observed formation of a series of perfluorocarboxylic acids during the simulated atmospheric oxidation of long-chain fluorinated alcohols[5] and are well supported by the literature data.

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