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COMMENT

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Comment on "Trifluoroacetic acid formation from HFC-134a under atmospheric conditions" by A. Vincent, K. Fujioka, Y. Luo, R. I. Kaiser and R. Sun, *Phys. Chem. Chem. Phys.*, 2026, 28, 4433

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Vincent *et al.*[1] report the results of a computational study of the formation of trifluoroacetic acid ($CF_3C(O)OH$, TFA) in the atmospheric degradation of HFC-134a (CF_3CFH_2). They find that "*both TFA and its precursor trifluoroacetyl fluoride ($CF_3C(O)F$) product forming channels have inaccessible energy barriers under atmospheric conditions. Although this research does not rule out the possibility that TFA can be formed from HFC-134a in the atmosphere, it casts doubt on the feasibility of the previous proposed mechanism*". The mechanism for the formation of $CF_3C(O)F$ is based on a large body of experimental and computational work[2–4] which can be represented by the following reactions.

$$CF_3CFH_2 + OH \rightarrow CF_3CFH + H_2O \quad (1)$$

$$CF_3CFH + O_2 + M \rightarrow CF_3CFHO_2 + M \quad (2)$$

$$CF_3CFHO_2 + NO \rightarrow CF_3CFHO^* + NO_2 \quad (3)$$

$$CF_3CFHO^* \rightarrow CF_3 + HC(O)F \quad (4)$$

$$CF_3CFHO^* + M \rightarrow CF_3CFHO + M \quad (5)$$

$$CF_3CFHO + M \rightarrow CF_3 + HC(O)F \quad (6)$$

$$CF_3CFHO + O_2 \rightarrow CF_3C(O)F + HO_2 \quad (7)$$

Vincent *et al.*[1] considered reactions (1)–(3) and concluded that the adduct formed in reaction (3) exclusively dissociates back to reactants. This conclusion is contrary to experimental data showing the formation of alkoxy radicals and NO_2 as products in this and all other reactions of peroxy radicals with NO.[2,4–7] As a result of their conclusion, they did not consider reactions (4)–(7), which are key to understanding the formation of TFA from HFC-134a in the atmosphere. Reaction (3) produces vibrationally excited CF_3CFHO^* radicals which can either decompose or undergo collisional stabilization. CF_3CFHO radicals can undergo thermal decomposition or reaction with O_2. The tropospheric fate of $CF_3C(O)F$ is uptake on water surfaces and hydrolysis to give TFA.[8,9] Vincent *et al.*[1] did not consider this process. The yield of $CF_3C(O)F$ and hence TFA in the atmospheric oxidation of HFC-134a is estimated to be 7–20%.[10] Computational studies of the reactions leading to TFA in the atmospheric degradation of HFC-134a are of interest. We look forward to follow-up studies that include the omitted reactions noted above.

Author contributions

All authors contributed to conceptualization, writing, reviewing, and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this Comment.

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