

Refrigerant Degradation: Is HFC-23 (CF₃H) formed due to the decomposition of HFOs and HCFOs in the troposphere?

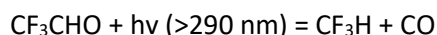
HFOs and HCFOs that contain the CF₃CH= group breakdown in the atmosphere to give CF₃CHO (trifluoroacetaldehyde) as an intermediate product. The main final breakdown products of HFOs containing the CF₃CH= moiety are HF, and CO₂. The main final breakdown products of HCFOs containing the CF₃CH= moiety are HF, HCl, and CO₂.

A recent paper¹ and presentation (Hansen^{i,ii}) has proposed that a minor product CF₃H is formed in yields of 11.0 ± 5.5 % from atmospheric photolysis of CF₃CHO at 308 nm (a wavelength relevant to the troposphere and corresponding to the maximum UV absorbance of CF₃CHO).

This is an entirely different conclusion to that made in an earlier published peer-reviewed paperⁱⁱⁱ that has been widely referenced in other atmospheric chemistry studies.^{iv}

Earlier Studies of CF₃CHO Photolysis

Investigations into the potential formation of CF₃H from CF₃CHO are not recent; the 1994 Ozone Assessment^v (Chapter 12), in its section on aldehydes, reported that the quantum yield for formation of CF₃H from CF₃CHO via the reaction:



is too low to significantly enhance the GWP of the parent compound.

Chiappero³ et. al. studied the photolysis and quantum yields of the fluoroaldehydes CF₃CHO, C₂F₅CHO, C₃F₇CHO and C₄F₉CHO at 254 nm and 308 nm wavelengths and stated “We conclude that formation of HFCs from the tropospheric photolysis of fluoroaldehydes is of no significance.” The Chiappero³ paper also concluded that “the 308 nm photolysis of CF₃CHO proceeds essentially exclusively via C-C bond scission,” a reaction route which does not produce CF₃H. The Chiappero paper also summarises earlier studies of fluorinated aldehyde photolysis.

HFOs and HCFOs are very short-lived substances (VSLs) with lifetimes measured in days, that are quickly removed by chemical degradation, predominantly in the troposphere. In the atmosphere, HFOs and HCFOs containing the CF₃CH= moiety produce the intermediate product CF₃CHO, which is formed in yields of up to 100% depending on the particular substance. It should be noted that HFOs that lack the CF₃CH= moiety, such as HFO-1234yf (CF₃CF=CH₂) do not form CF₃CHO in their atmospheric reactions.

¹ At the time of writing this EFCTC analysis, the paper is a preprint that has not been peer reviewed

According to these past studies, the dominant atmospheric fate of CF₃CHO is photolysis, resulting in a short atmospheric lifetime for CF₃CHO: Chiappero, et. al.³ provide lifetimes of CF₃CHO with respect to photolysis in the atmosphere at different altitudes, and based on this work, Andersen, et. al.^{vi} state that the dominant fate of CF₃CHO is photolysis resulting in an estimated atmospheric lifetime of ≤2 days, and Rattigan, et. al.^{vii} estimate a photolytic lifetime for CF₃CHO on the order of 4 hours.

In summary, previous studies reported in peer-reviewed journals have concluded that CF₃CHO is removed from the troposphere via photolysis, leading to CO₂ and HF as the final breakdown products and, to a lesser extent, reaction with OH radicals (Chiappero, et. al.³):

Photolysis of CF₃CHO gives CF₃ and HCO radicals. CF₃ radicals will add O₂ to give CF₃OO radicals which are then converted into COF₂ (Wallington et al.^{viii}) which hydrolyzes to give CO₂ and HF. Hence, the ultimate photolysis products of CF₃CHO are HF and CO₂.

Reaction of CF₃CHO with OH radicals gives CF₃CO radicals, which will add O₂ to give CF₃C(O)OO radicals, the majority of which will be converted into COF₂, which hydrolyzes to HF and CO₂. A small fraction of CF₃C(O)OO radicals may be converted into CF₃C(O)OH via reaction with HO₂ radicals under low NO_x atmospheric conditions (Hurley et al.^{ix}). Hence the major products of the reaction of CF₃CHO with OH radicals are CO₂ and HF.

The Hansen Paper

The Hansen paper¹ in its conclusion states that “more research is needed measuring the wavelength and pressure dependence of quantum yields for R1 [CF₃CHO → CF₃ + CHO] and R2 [CF₃CHO → CF₃H + CO] for CF₃CHO explicitly and we call for urgent experiments in this regard.” However, as discussed above, the Chiappero paper³ had already investigated CF₃CHO quantum yields for reaction routes R1 and R2 at different wavelengths and concluded that “the 308 nm photolysis of CF₃CHO proceeds essentially exclusively via C-C bond scission,”, i.e., proceeds exclusively via reaction route R1, which does not produce CF₃H. As also discussed above, the Chiappero paper has been widely referenced in other atmospheric chemistry studies.

Box 1 has relevant extracts from the Chiappero paper, with key text highlighted, discussing their experimental method resulting in the conclusion that formation of HFCs [CF₃H] from the tropospheric photolysis of fluoroaldehydes [CF₃CHO] is of no significance. Box 1 also has observations on their experimental method.

Box 2 has relevant extracts from the Hansen paper with key text highlighted and has observations on their experimental method used from which they inferred the formation of CF₃H from CF₃CHO from tropospheric photolysis. In addition, it is also critical to note that the Hansen experiment uses CO detection to indirectly derive the CF₃H formation yield. Further measurements may be required to establish if CF₃H is actually formed and the mechanism of its formation.

Box 1: Formation CF₃H from the tropospheric photolysis of CF₃CHO is of no significance

Chiappero, et. al., Atmospheric Chemistry of Perfluoroaldehydes (C_xF_{2x+1}CHO) and Fluorotelomer Aldehydes (C_xF_{2x+1}CH₂CHO): Quantification of the Important Role of Photolysis

Paper Extract

At 308 nm: As discussed in section 2.1, NO was added to the gas mixtures to scavenge the photolysis products and avoid loss of aldehydes by unwanted chemistry. The photolysis of CF₃CHO is expected to give CF₃ radicals which, *in the absence of NO*, may abstract hydrogen from CF₃CHO leading to formation of CF₃H and additional loss of CF₃CHO. **Formation of CF₃H in this process could be confused with the direct formation of this product as a primary photolysis product.** CF₃H has a long tropospheric lifetime, a large global warming potential, and if formed as a product of the atmospheric photolysis of CF₃CHO would be of significance. Figure 8 shows a plot of the formation of CF₃NO versus loss of CF₃CHO observed following the pulsed radiolysis of CF₃CHO/NO/N₂ mixtures. The line through the data gives a CF₃NO yield of 98 ± 7%.

Features attributable to CF₃H were searched for but not found, and an upper limit of <2% was established for the yield of this species. The observation of CF₃NO product in a yield which is indistinguishable from 100% is consistent with expectations based upon analogy with CH₃CHO that the 308 nm photolysis of CF₃CHO proceeds essentially exclusively via C-C bond scission.

In similar experiments [at 308 nm] involving C₂F₅CHO, C₃F₇CHO, and C₄F₉CHO, there was no evidence (<5% yield) for the formation of C₂F₅H, C₃F₇H, and C₄F₉H. **We conclude that formation of HFCs from the tropospheric photolysis of fluoroaldehydes is of no significance.**

The experiments were carried out at close to atmospheric pressure. Reaction mixtures consisted of 1-5 Torr of the carbonyl compound and 10-50 Torr of NO in 700 Torr of N₂ diluent. NO was added to scavenge the radical products formed in the photodissociation of the carbonyl compound, which might otherwise contribute to unwanted secondary loss of the carbonyl compound.

The photolysis of CF₃CHO has been studied previously by Dodd and Smith, Pearce and Whytock, Morris and Thynne, Richter et al., and Sellevåg et al. Dodd and Smith used 313 nm photolysis light and estimated quantum yields of 0.021 for the CF₃H + CO channel and 0.12 for the CF₃ + HCO channel. The quantum yield for CF₃H formation of 0.021 is slightly larger than the upper limit of <0.02 derived in the present work. The combined quantum yield reported by Dodd and Smith is plotted in Figure 12 and is consistent with the results from the present work. Pearce and Whytock investigated the CF₃H + CO channel (313 nm photolysis light) and concluded that it had a quantum yield of zero. Pearce and Whytock ascribed the discrepancy between their result and that of Dodd and Smith to either errors in the light intensity calibration or the presence of photolysis light of wavelengths <313 nm in the study by Dodd and Smith.

The Chiappero paper states:

We conclude that formation of HFCs [CF₃H] from the tropospheric photolysis of fluoroaldehydes [CF₃CHO] is of no significance.

Observations on the Chiappero paper

The paper describes carefully designed experiments to detect the formation of CF₃H in this process at 308 nm but none was detected. The experimental method appears to be robust as it does result in the formation of CF₃H via the reaction CF₃CHO → CF₃H + CO at wavelengths not relevant to the troposphere (i.e., at 254 nm).

Box 1: Observations on formation of CF₃H from CF₃CHO from tropospheric photolysis

Photodissociation of CF₃CHO provides a new source of CHF₃ (HFC-23) in the atmosphere: implications for new refrigerants – Hansen paper

How the paper detects that CF₃H is formed. In brief, a molecular beam of 2% CF₃CHO or CH₃CHO in helium was passed into a VMI spectrometer. The early time component of this beam was intersected by a photolysis laser (308 nm), followed by an ionisation (detection) laser. Radical fragments (CF₃/CH₃ and CHO) from R1 [Photolytic cleavage of the C=C bond giving CF₃ and CHO] were probed at 115 nm to ionise all quantum states of the radical of interest. **CO from R2 [photolytic decarbonylation] was detected in specific quantum states at ~230 nm via REMPI.** Nascent ions were separated in a time-of-flight mass spectrometer before impacting a position-sensitive MCP/phosphor screen detector, from which a kinetic energy distribution was determined. **This is a collision free method that interrogates the unimolecular photochemistry of isolated molecules, providing true zero-pressure measurements. Supplementary FT-IR experiments were conducted in a standard gas cell to establish an upper limit for the formation of CO from the triple fragmentation channel (R3) following in situ photolysis at 308 nm.**

The Hansen paper concludes: In this paper, we demonstrate that CF₃CHO photolyses to form HFC-23. Although the quantum yield is small, this pathway could account for the fate of 11.0 ± 5.5 % of atmospheric CF₃CHO.

Observations on the Hansen paper

The experiment utilizes acetaldehyde as the reference compound and as the basis of the authors' conclusions although the available data for acetaldehyde from previous studies are very poorly defined and are subject to large uncertainties. **Although international atmospheric science experts (JPL/NASA and IUPAC kinetic data evaluation panels) recommend a zero yield of CO for acetaldehyde photolysis at ≥ 294 nmⁱⁱ, the authors chose to use a non-zero yield for CO from acetaldehyde.** The authors claim a nearly-constant non-zero yield of CO for acetaldehyde photolysis at longer wavelengths (>300 nm), which is a non-realistic representation, i.e. the quantum yield of *any* products from acetaldehyde or fluorinated aldehydes is expected to decrease with increasing wavelength. In fact, the Hansen paper acknowledges that "there are too many uncertainties at present. The most significant uncertainty is using quantum yields from CH₃CHO as a proxy for CF₃CHO, despite the similarity shown in Fig. 4".

The experimental conditions, specifically pressure, are not relevant to real atmospheric conditions, and an extrapolation of the experimental observations may lead to erroneous conclusions and large uncertainties. The experiments were performed under collision-less conditions (zero pressure), which are not representative of atmospheric conditions. Upon photolysis, CF₃CHO is initially transformed into an excited state. The excited molecule can then undergo intramolecular rearrangement to form CO + CF₃H, but under atmospheric (i.e. collision) conditions, the excited state molecule can be quenched by collision with another molecule rather than rearranging to CF₃H and CO. In the absence of the opportunity to quench the excited state via a collision with another molecule, there is more opportunity for intramolecular rearrangement forming CF₃H under the conditions of the Hansen experiment. The authors must assume that their observations still apply to real atmospheric conditions (pressure) to draw any relevant conclusions. This may introduce a large uncertainty to the overall data and conclusions. In addition, it is also critical to note that the Hansen experiment uses CO detection to indirectly derive the CF₃H formation yield. Further measurements may be required to establish if CF₃H is actually formed and the mechanism of its formation.

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About EFCTC

The European FluoroCarbons Technical Committee is a Cefic Sector Group that monitors legislation related to HFCs (hydrofluorocarbons), and HFOs (hydrofluoro-olefins) in the EU and at global level.

Fluorocarbons are used as feedstock, as refrigerants, as solvents and as blowing agents for insulation plastic foams.

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