Published evidence supports very low yield of TFA from most HFOs and HCFOs

Summary

EFCTC has analysed the most current, peer reviewed scientific papers on the potential contribution of HFOs and HCFOs, containing the CF_3CH= moiety, to existing and future TFA levels. **The conclusion from these papers is that the very low yields of TFA from these substances mean that their expected contribution to TFA in the environment is extremely small.**

In addition, and taking into account a wider number of substances, the UNEP Environmental Effects Assessment Panel, in its Summary Update 2020 for Policymakers [5], summarised these scientific conclusions for TFA: *The current low concentration of trifluoroacetic acid (TFA) produced by the degradation of several hydrofluorocarbons (HFCs) and hydrofluoro-olefins (HFOs), is currently judged not to pose a risk to human health or to the environment.*

This EFCTC analysis is in response to the UBA report on *Persistent degradation products of halogenated refrigerants.*

In the EU the substances with the CF_3CH= moiety reported as supplied on the EU market are HFO-1234ze, HFO-1336mzz and HCFO-1233zd.

Atmospheric breakdown of HFOs and HCFOs containing the CF_3CH= moiety

In the atmosphere, HFOs and HCFOs containing the CF_3CH= moiety, have a hydrogen on the central carbon atom, and produce the intermediate breakdown product CF_3CHO, which is formed in yields of up to 100% depending on the specific substance. These include HFO-1234ze, HFO-1336mzz and HCFO-1233zd(E). The WMO 2014 Ozone Report [1] states *"On the other hand, if there is a hydrogen on the central carbon atom there is no TFA formation, such as in CF_3CH=CHF (HFO-1234ze) or CF_3CH=CHCl (trans-1-chloro-3,3,3-trifluoropropylene or tCFP; also referred to as HFO-1233zd).*

A more recent 2018 paper "A three-dimensional model of the atmospheric chemistry of E- and Z-CF_3CH=CHCl (HCFO-1233(zd) (E/Z))" [2] incorporates the most up-to-date atmospheric chemistry of the relevant fluorinated species and concludes that the average global yield of TFA from atmospheric processing of E-CF_3CH=CHCl is approximately 2%. This paper provides a good basis for understanding the degradation of other HFOs and HCFOs with a CF_3CH= group, via CF_3CHO with yields of TFA expected to be similar, in the range about 0% to 2%. In addition, for HFO-1336mzz(Z), which break down in the atmosphere to produce up to 2 molecules of CF_3CHO [3], the yield of TFA is expected to be in the range about 0% to 4%. However, it should be noted that the lifetime of each HFO/HCFO and location of emissions does affect where CF_3CHO will be formed and, under what conditions it will decompose to other products.

In summary, the very low yields of TFA from these HFOs and HCFO-1233zd(E) mean that their expected contribution to TFA in the environment is extremely small [4]. In addition, and taking into account a wider number of substances, the UNEP Environmental Effects Assessment Panel, in its

EFCTC
Rue Belliard 40, Box 15, B-1040 Brussels
Tel. +32.2.436.95.06 anc@cefic.be www.fluorocarbons.org
EU Transparency Register n° 64879142323-90

Summary Update 2020 for Policymakers [5], summarised these scientific conclusions for TFA: *The current low concentration of trifluoroacetic acid (TFA) produced by the degradation of several hydrofluorocarbons (HFCs) and hydrofluoro-olefins (HFOs), is currently judged not to pose a risk to human health or to the environment.*

Surprisingly, the UBA report on *Persistent degradation products of halogenated refrigerants* [6] comes to a different conclusion, based on the earlier WMO 2010 report [7] and not based on the more recent WMO 2014 report [1] or the 2018 paper [2]. The UBA report concluded that *"Based on the above data, the TFA formation potential of substances that form trifluoroacetaldehyde as an intermediate is not generally assumed to be zero in this study. Instead, the TFA yield is calculated within the range given in the WMO 2010 Ozone Report (WMO 2010), assuming a possible TFA formation rate of up to 10 %. However, this rate of formation could also be higher. The lack of clear indications in the literature prevents a more exact estimation of the TFA formation rate."* In addition, the UBA report appears to accept the 2% TFA yield from HCFO-1233zd reported in the 2018 paper [2], and uses this for its TFA emissions estimates, but then ignores the 2018 paper as a basis for estimating TFA yields for the related HFOs that also breakdown via CF_3CHO.

Discussion of atmospheric degradation of CF_3CHO resulting in very low yields of TFA

The 2018 paper "A three-dimensional model of the atmospheric chemistry of E- and Z-CF_3CH=CHCl (HCFO-1233(zd) (E/Z))" [2] in the supplemental information, provides a detailed summary of the atmospheric chemistry of CF_3CHO and discusses all three degradation routes for CF_3CHO (that are also listed in the UBA report [6]). The atmospheric model explicitly includes this chemistry. This paper provides a good basis for understanding the degradation via CF_3CHO of the other HFOs and HCFOs with a CF_3CH= group, but it should be noted that the lifetime of each HFO/HCFO and location of emissions does affect where CF_3CHO will be formed and, under what conditions it will decompose to other products.

The atmospheric degradation of CF_3CHO can occur via three routes, with their reaction rates dictating their relative contribution and the overall yield of TFA. The route(s) with the highest reaction rate resulting in the shortest atmospheric lifetime will dominate.

Summary of degradation routes for CF_3CHO

Degradation Route	Atmospheric Lifetime	Reaction	Comment
Major: Photolysis	0.92-2.5 days [8]; 19 hours [9].	$CF_3CHO + h\nu \rightarrow CF_3 + CHO$	Does not form TFA, with HF and CO_2 as final products.
Minor: Hydroxyl radical OH	26 days [10]	$CF_3CHO + OH \rightarrow CF_3CO + H_2O$	Produces low yield of TFA following further reaction of the acyl radical (CF_3CO). The low yield of TFA is influenced by atmospheric concentration of NOx. In the presence of excess NO, no TFA was detected [11]
Minor:	Homogeneous gas-phase reaction with	$CF_3CHO + H_2O \Leftrightarrow CF_3CH(OH)_2$	The hydrate is in equilibrium with CF_3CHO [13]

EFCTC
Rue Belliard 40, Box 15, B-1040 Brussels
Tel. +32.2.436.95.06 anc@cefic.be www.fluorocarbons.org
EU Transparency Register n° 64879142323-90

Hydration then OH radical	H_2O occurs slowly, if at all. Typical lifetime around 15 days [12] for contact with water-rich media such as clouds	$CF_3CH(OH)_2$ +OH +O_2 → CF_3COOH	Estimated atmospheric lifetime for reaction of $CF_3CH(OH)_2$ with OH of approximately 90 days [13]. The 90 days lifetime is long enough to allow competition from the likely dehydration under low humidity conditions and subsequent fast loss via photolysis. If the hydrate reacts with OH, the yield of TFA is 100% [13]

Note: The lifetime of each HFO/HCFO and location of emissions does affect to some extent where CF_3CHO will be formed and, under what conditions it will decompose to other products.

Major Route: Photolysis

$CF_3CHO + h\nu \rightarrow CF_3 + CHO$ → via several steps COF_2+ HF → CO_2 +3HF

Photolysis of CF_3CHO in the troposphere gives CF_3 and HCO radicals. CF_3 radicals will add O_2 to give CF_3OO radicals which are then converted into COF_2 [14] which hydrolyzes to give CO_2 and HF. Hence, the ultimate photolysis products of CF_3CHO are HF and CO_2. This route does not form TFA.

The photolytic lifetime of CF_3CHO can vary to some extend based on local conditions. Chiappero *et al.* [8 6] reported an estimated photochemical lifetime of 0.92-2.5 days, for altitudes 11.7 and 0 km. Calvert et al. [9] estimate the photochemical lifetime for an overhead sun in the lower troposphere to be approximately 19 hours, based on calculations using the quantum yield of 0.17 from [8].

Minor Route: Reaction with hydroxyl radical OH

CF_3CHO +OH → CF_3CO +H_2O → via several steps CF_3COOH (<10% from CF_3CO radicals)

Reaction with OH, which is of lesser importance, but also represents a sink for CF_3CHO, gives CF_3CO radicals [15]. The atmospheric degradation routes by which CF_3CO radicals can be transformed into CF_3COOH (TFA) as a minor product from this route have been documented. TFA yield is <10% from CF_3CO radicals, which in turn is a minor route from CF_3CHO [16]. A lifetime of approximately 26 days was determined, significantly longer than the photolytic lifetime [10].

The 2018 paper "A three-dimensional model of the atmospheric chemistry of E- and Z-CF_3CH=CHCl (HCFO-1233(zd) (E/Z))" [2] takes into account NOx chemistry in its 3D model.

Reaction of OH radicals with CF_3CHO proceeds via hydrogen atom abstraction to give $CF_3C(O)$ radicals. The atmospheric fate of $CF_3C(O)$ radicals is addition of O_2 to give the corresponding acyl peroxy radicals. In the presence of excess NO the fate of the acyl peroxy radicals is reaction to give acetoxy radicals, $CF_3C(O)O$, which will eliminate CO_2 leading to HF and CO_2 formation. No evidence for the formation of perfluorocarboxylic acids (TFA) was found in the experiments. It was concluded that the OH radical initiated gas-phase atmospheric oxidation of perfluoroaldehydes (including CF_3CHO) *in the presence of excess NO* is not a significant source of perfluorocarboxylic acids (TFA). However, it should

EFCTC
Rue Belliard 40, Box 15, B-1040 Brussels
Tel. +32.2.436.95.06 anc@cefic.be www.fluorocarbons.org
EU Transparency Register n° 64879142323-90

be noted that in *absence of NOx*, perfluorocarboxylic acid formation (TFA) is observed during the Cl atom initiated oxidation CF_3CHO [11] (and similar results are expected for OH radical initiated oxidation).

HFOs/HCFOs have very short lifetimes (days) and are not evenly distributed in the troposphere before decomposition. Decomposition closer to emission sources (usually populated regions), typically in regions where NOx chemistry may dominate, is expected to decrease the yield of TFA significantly. HFO-1234ze and HFO-1336mzz(Z) (with $CF_3CH=$ group) have similar atmospheric lifetimes to HCFO-1233ze(E&Z isomers) suggesting similar TFA yields from CF_3CHO, but dependent on the lifetime of each HFO/HCFO and location of emissions.

Minor Route: Hydration followed by reaction with hydroxyl radical

$CF_3CHO + H_2O \Leftrightarrow CF_3CH(OH)_2$

The hydration of CF_3CHO produces $CF_3CH(OH)_2$ in a reversible reaction in the atmosphere, but this requires contact with water-rich media such as clouds. A typical lifetime for uptake into aqueous droplets is about 15 days [12]. Homogeneous gas-phase reaction with H_2O occurs slowly, if at all. The $CF_3CH(OH)_2$ if available in the atmosphere can react with hydroxyl radicals leading to TFA in 100% yield. This reaction is slow with an estimated atmospheric lifetime for reaction of $CF_3CH(OH)_2$ with OH of approximately 90 days [13]. However, as the CF_3CHO and $CF_3CH(OH)_2$ are in equilibrium, the assumption that CF_3CHO once hydrated goes to 100% TFA cannot be substantiated. The 90 days lifetime for reaction of $CF_3CH(OH)_2$ with OH is long enough to allow competition from the likely dehydration under low humidity conditions and subsequent fast loss via photolysis. Therefore, the probability of $CF_3CH(OH)_2$ dehydration to CF_3CHO under low humidity conditions and subsequent photolysis suggest that the hydration path may not contribute to TFA formation. It should be noted that the equilibrium constants and their dependence on temperature are not known [15].

References

[1] WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project – Report No. 55, Chapter 5, section 5.2.5.
[2] A three-dimensional model of the atmospheric chemistry of E and ZCF3CH=CHCl (HCFO-1233(zd) (E/Z)) Mads P. Sulbaek Andersen, Johan A. Schmidt, Aleksandra Volkova, Donald J. Wuebbles, Atmospheric Environment 179 (2018) 250–259. See the Supplemental Information which summaries the atmospheric chemistry used in the model.
[3] Atmospheric chemistry of E-$CF_3CH=CHCF_3$: Reaction kinetics of OH radicals and products of OH-initiated oxidation, Feiyao Qing, Qin Guo, Liang Chen, Hengdao Quan, Junji Mizukado Chemical Physics Letters 706 (2018) 93–98
[4] The EEA report No 15/2020 Fluorinated greenhouse gases 2020 in Table A5.17 lists four HFOs and HCFOs supplied in the EU in 2019. These are HFO-1234ze, HFO-1336mzz, HCFO-1233zd and HFO-1234yf. The first 3 have the $CF_3CH=$ moiety.
[5] Available at Environmental Effects Assessment Panel (EEAP) | Ozone Secretariat (unep.org)
[6] UBA Final report Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential | Umweltbundesamt. See section 2.7.3.2.
[7] World Meteorological Organization Global Ozone Research and Monitoring Project—Report No. 52 Scientific Assessment of Ozone Depletion: 2010.

EFCTC
Rue Belliard 40, Box 15, B-1040 Brussels
Tel. +32.2.436.95.06 anc@cefic.be www.fluorocarbons.org
EU Transparency Register n° 64879142323-90

[8] Malisa S. Chiappero, Fabio E. Malanca, Gustavo A. Arguello, Steven T. Wooldridge, Michael D. Hurley, James C. Ball, Timothy J. Wallington, Robert L. Waterland, and Robert C. Buck J. Phys. Chem. A 2006, 110, 11944-11953, Atmospheric Chemistry of Perfluoroaldehydes (CxF2x+1CHO) and Fluorotelomer Aldehydes (CxF2x+1CH_2CHO): Quantification of the Important Role of Photolysis.

[9] Calvert, J. G., R. G. Derwent, J. J. Orlando, G. S. Tyndall & T. J. Wallington (2008): Mechanisms of Atmospheric Oxidation of the Alkanes. Oxford University Press, Oxford, New York.

[10] Sellevag, S.R., Kelly, T., Sidebottom, H., Nielsen, C.J., 2004. A study of the IR and UV-Vis absorption cross-sections, photolysis and OH-initiated oxidation of CF_3CHO and CF_3CH_2CHO. Phys. Chem. Chem. Phys. 6, 1243–1252. doi:10.1039/B315941H

[11] M. P. Sulbaek Andersen, O. J. Nielsen, M. D. Hurley, J. C. Ball, T. J. Wallington and J. E. Stevens, Atmospheric Chemistry of n-CxF2x+1CHO (x= 1, 3, 4): Reaction with Cl Atoms, OH Radicals and IR Spectra of CxF2x+1C(O)O_2NO_2, J. Phys. Chem. A 2004, 108, 5189-5196.

[12] Atmospheric Degradation of Ozone Depleting Substances, Their Substitutes, and Related Species, James B. Burkholder, R. A. Cox, and A. R. Ravishankara, Chem. Rev. 2015, 115, 3704−3759, DOI: 10.1021/cr5006759, see section 7.1.1.

[13] Atmospheric Chemistry of Perfluorinated Aldehyde Hydrates (n-CxF2x+1CH$(OH)_2$, x= 1, 3, 4): Hydration, Dehydration, and Kinetics and Mechanism of Cl Atom and OH, Radical Initiated Oxidation, M. P. Sulbaek Andersen, A. Toft, O. J. Nielsen, M. D. Hurley, T. J. Wallington, H. Chishima, K. Tonokura, S. A. Mabury, J. W. Martin, and D. A. Ellis, J. Phys. Chem. A 2006, 110, 9854-9860.

[14] Wallington, T. J., Schneider, W. F., Worsnop, D. R., Nielsen, O. J., Sehested, J., DeBruyn, W., and Shorter, J. A.: The environmental impact of CFC replacements-HFCs and HCFCs, Environ. Sci. Technol., 28, 320A–326A, 1994.

[15] Sulbaek Andersen, M.P., Stenby, C., Nielsen, O.J., Hurley, M.D., Ball, J.C., Wallington, T.J., Martin, J.W., Ellis, D.A., Mabury, S.A., 2004. Atmospheric Chemistry of n-CxF2x+1CHO (x=1, 3, 4): Mechanism of the CxF2x+1C(O)O_2 + HO_2 Reaction. J. Phys. Chem. A 108, 6325–6330.

[16] Ellis, D.A., Martin, J.W., De Silva, A.O., Mabury, S.A., Hurley, M.D., Sulbaek Andersen, M.P., Wallington, T.J., 2004. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. Environ. Sci. Technol. 38, 3316–3321. doi:10.1021/es049860w.

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.

Contact: EFCTC Chairman: Dr. Nick Campbell, nick.campbell@arkema.com
EFCTC Secretariat: Angelica Candido, anc@cefic.be

EFCTC
Rue Belliard 40, Box 15, B-1040 Brussels
Tel. +32.2.436.95.06 anc@cefic.be www.fluorocarbons.org
EU Transparency Register n° 64879142323-90