

## 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  $\text{CF}_3\text{CH=}$  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  $\text{CF}_3\text{CH=}$  moiety reported as supplied on the EU market are HFO-1234ze, HFO-1336mzz and HCFO-1233zd.

### Atmospheric breakdown of HFOs and HCFOs containing the $\text{CF}_3\text{CH=}$ moiety

In the atmosphere, HFOs and HCFOs containing the  $\text{CF}_3\text{CH=}$  moiety, have a hydrogen on the central carbon atom, and produce the intermediate breakdown product  $\text{CF}_3\text{CHO}$ , 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  $\text{CF}_3\text{CH=CHF}$  (HFO-1234ze) or  $\text{CF}_3\text{CH=CHCl}$  (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- $\text{CF}_3\text{CH=CHCl}$  (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- $\text{CF}_3\text{CH=CHCl}$  is approximately 2%. This paper provides a good basis for understanding the degradation of other HFOs and HCFOs with a  $\text{CF}_3\text{CH=}$  group, via  $\text{CF}_3\text{CHO}$  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  $\text{CF}_3\text{CHO}$  [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  $\text{CF}_3\text{CHO}$  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

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<sub>3</sub>CHO.

### Discussion of atmospheric degradation of CF<sub>3</sub>CHO resulting in very low yields of TFA

The 2018 paper “A three-dimensional model of the atmospheric chemistry of E- and Z-CF<sub>3</sub>CH=CHCl (HCFO-1233(zd) (E/Z))” [2] in the supplemental information, provides a detailed summary of the atmospheric chemistry of CF<sub>3</sub>CHO and discusses all three degradation routes for CF<sub>3</sub>CHO (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<sub>3</sub>CHO of the other HFOs and HCFOs with a CF<sub>3</sub>CH= group, but it should be noted that the lifetime of each HFO/HCFO and location of emissions does affect where CF<sub>3</sub>CHO will be formed and, under what conditions it will decompose to other products.

The atmospheric degradation of CF<sub>3</sub>CHO 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.

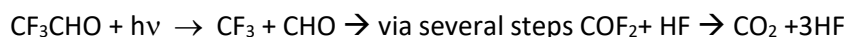
### Summary of degradation routes for CF<sub>3</sub>CHO

Degradation Route	Atmospheric Lifetime	Reaction	Comment
<b>Major:</b> Photolysis	0.92-2.5 days [8]; 19 hours [9].	CF <sub>3</sub> CHO + hv → CF <sub>3</sub> + CHO	Does not form TFA, with HF and CO <sub>2</sub> as final products.
<b>Minor:</b> Hydroxyl radical OH	26 days [10]	CF <sub>3</sub> CHO + OH → CF <sub>3</sub> CO + H <sub>2</sub> O	Produces low yield of TFA following further reaction of the acyl radical (CF <sub>3</sub> CO).  The low yield of TFA is influenced by atmospheric concentration of NO <sub>x</sub> . In the presence of excess NO, no TFA was detected [11]
<b>Minor:</b>	Homogeneous gas-phase reaction with	CF <sub>3</sub> CHO + H <sub>2</sub> O ⇌ CF <sub>3</sub> CH(OH) <sub>2</sub>	The hydrate is in equilibrium with CF <sub>3</sub> CHO [13]

<b>Hydration then OH radical</b>	<p>H<sub>2</sub>O occurs slowly, if at all.</p> <p>Typical lifetime around 15 days [12] for contact with water-rich media such as clouds</p>	$\text{CF}_3\text{CH}(\text{OH})_2 + \text{OH} + \text{O}_2 \rightarrow \text{CF}_3\text{COOH}$	<p>Estimated atmospheric lifetime for reaction of CF<sub>3</sub>CH(OH)<sub>2</sub> 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.</p> <p>If the hydrate reacts with OH, the yield of TFA is 100% [13]</p>
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Note: The lifetime of each HFO/HCFO and location of emissions does affect to some extent where CF<sub>3</sub>CHO will be formed and, under what conditions it will decompose to other products.

### Major Route: Photolysis



Photolysis of CF<sub>3</sub>CHO in the troposphere gives CF<sub>3</sub> and HCO radicals. CF<sub>3</sub> radicals will add O<sub>2</sub> to give CF<sub>3</sub>OO radicals which are then converted into COF<sub>2</sub> [14] which hydrolyzes to give CO<sub>2</sub> and HF. Hence, the ultimate photolysis products of CF<sub>3</sub>CHO are HF and CO<sub>2</sub>. This route does not form TFA.

The photolytic lifetime of CF<sub>3</sub>CHO can vary to some extent 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



Reaction with OH, which is of lesser importance, but also represents a sink for CF<sub>3</sub>CHO, gives CF<sub>3</sub>CO radicals [15]. The atmospheric degradation routes by which CF<sub>3</sub>CO radicals can be transformed into CF<sub>3</sub>COOH (TFA) as a minor product from this route have been documented. TFA yield is <10% from CF<sub>3</sub>CO radicals, which in turn is a minor route from CF<sub>3</sub>CHO [16]. A lifetime of approximately 26 days was determined, significantly longer than the photolytic lifetime [10].

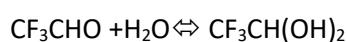
The 2018 paper "A three-dimensional model of the atmospheric chemistry of E- and Z-CF<sub>3</sub>CH=CHCl (HCFO-1233(zd) (E/Z))" [2] takes into account NO<sub>x</sub> chemistry in its 3D model.

Reaction of OH radicals with CF<sub>3</sub>CHO proceeds via hydrogen atom abstraction to give CF<sub>3</sub>C(O) radicals. The atmospheric fate of CF<sub>3</sub>C(O) radicals is addition of O<sub>2</sub> 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<sub>3</sub>C(O)O, which will eliminate CO<sub>2</sub> leading to HF and CO<sub>2</sub> 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<sub>3</sub>CHO) *in the presence of excess NO* is not a significant source of perfluorocarboxylic acids (TFA). However, it should

be noted that in *absence of NO<sub>x</sub>*, perfluorocarboxylic acid formation (TFA) is observed during the Cl atom initiated oxidation CF<sub>3</sub>CHO [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 NO<sub>x</sub> chemistry may dominate, is expected to decrease the yield of TFA significantly. HFO-1234ze and HFO-1336mzz(Z) (with CF<sub>3</sub>CH= group) have similar atmospheric lifetimes to HCFO-1233ze(E&Z isomers) suggesting similar TFA yields from CF<sub>3</sub>CHO, but dependent on the lifetime of each HFO/HCFO and location of emissions.

#### Minor Route: Hydration followed by reaction with hydroxyl radical



The hydration of CF<sub>3</sub>CHO produces CF<sub>3</sub>CH(OH)<sub>2</sub> 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<sub>2</sub>O occurs slowly, if at all. The CF<sub>3</sub>CH(OH)<sub>2</sub> 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<sub>3</sub>CH(OH)<sub>2</sub> with OH of approximately 90 days [13]. However, as the CF<sub>3</sub>CHO and CF<sub>3</sub>CH(OH)<sub>2</sub> are in equilibrium, the assumption that CF<sub>3</sub>CHO once hydrated goes to 100% TFA cannot be substantiated. The 90 days lifetime for reaction of CF<sub>3</sub>CH(OH)<sub>2</sub> 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<sub>3</sub>CH(OH)<sub>2</sub> dehydration to CF<sub>3</sub>CHO 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].

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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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