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Main Manuscript for

Ozonolysis can produce long-lived greenhouse gases from commercial refrigerants.

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This PDF file includes:

Main Text
Scheme 1
Figures 1 to 4

Abstract

Hydrofluoroolefins are being adopted as sustainable alternatives to long-lived fluorine- and chlorine-containing gases, and are finding current or potential mass-market applications as refrigerants, among a myriad of other uses. Their olefinic bond affords relatively rapid reaction with hydroxyl radicals present in the atmosphere, leading to short lifetimes and proportionally small global warming potentials. However, this type of functionality also allows reaction with ozone, and whilst these reactions are slow, we show that the products of these reactions can be extremely long-lived. Our chamber measurements show that several industrially important hydrofluoroolefins produce CHF₃ (fluoroform, HFC-23), a potent, long-lived greenhouse gas. When this process is accounted for in atmospheric chemical and transport modeling simulations, we find that the total radiative effect of certain compounds can be several times that of the direct radiative effect currently recommended by the World Meteorological Organization. Our supporting quantum chemical calculations indicate that a large range of exothermicity is exhibited in the initial stages of ozonolysis, which has a powerful influence on the CHF₃-yield. Furthermore, we identify certain molecular configurations that preclude the formation of long-lived greenhouse gases. This demonstrates the importance of product quantification and ozonolysis kinetics in determining the overall environmental impact of hydrofluoroolefin emissions.

Significance Statement

As societies phase-out long-lived and polluting halocarbons in favor of shorter-lived alternatives, novel chemicals are entering our environment. Hydrofluoroolefins (HFOs) are one such alternative. HFOs react rapidly with OH, the main atmospheric oxidant, implying minimal global warming potentials (GWPs). However, their olefinic bond also affords reaction with ozone. We measured the reactivity of five HFOs towards ozone, three of which were found to produce an extremely long-lived by-product, trifluoromethane. When these data are included in an atmospheric chemical transport model, GWPs are shown to increase several-fold, especially over longer time-horizons, demonstrating that a seemingly minor oxidation channel can be impactful.

Main Text

Introduction

Since their first commercial production in the 1930s, fluorinated gases (F-gases) have found many applications. First-generation F-gases, the chlorofluorocarbons (CFCs), presented low toxicity/flammability alternatives to incumbent refrigerants, but depleted stratospheric ozone catastrophically(1) and their long atmospheric lifetimes and high radiative efficiency led to large global warming potentials (GWPs)(2). CFCs were replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) that possessed much smaller or negligible ozone depletion potentials (ODPs), but their long atmospheric lifetimes (hundreds of years in some cases) also resulted in high GWPs(2). In recognition of this, the Kigali amendment to the Montreal Protocol will precipitate the phase-down of these chemicals, which will be replaced by shorter-lived alternatives(3).

Hydrofluoroolefins (HFOs) represent a promising alternative to HFCs, since their olefinic bond reacts rapidly with hydroxyl radicals in the atmosphere, leading to short lifetimes of days to weeks. These reactions generate carbonyl products, which readily hydrolyze, prompting removal from the atmosphere(4), and these products are therefore unimportant in determining overall GWPs of HFOs(5).

However, olefinic bonds also react with ozone (O₃) and despite possessing much smaller rate coefficients, higher atmospheric mixing ratios of O₃ allow ozonolysis to act as a sink for HFOs in

the environment. The ozonolysis mechanism is distinguished by its production of Criegee intermediates (CIs), energy-rich transient species that can participate in a multitude of unimolecular and bimolecular reactions(6), some of which could yield extremely long-lived products.

Previous studies on alkene ozonolysis have identified reaction channels that lead to the formation of short-chain hydrocarbons(7–10). Methane (CH₄) production in these systems is attributed to the “hot acid” channel, which operates when the acetaldehyde oxide CI engages in 1,3-ring closure forming 3-methyldioxirane, which isomerizes to acetic acid, formed with sufficient internal energy that it decomposes towards CH₄ and CO₂ via decarboxylation (see Scheme 1)(11) Here we propose that an analogous CHF₃-producing mechanism occurs for 2,2,2-trifluoroacetaldehyde oxide (TFAO), a CI that is produced in the ozonolysis of a subset of HFOs possessing substitution of CF₃ and hydrogen onto the same olefinic carbon atom, a commonplace motif among commercial F-gases, e.g. HFO-1234ze(*E/Z*), HCFO-1233zd(*E/Z*), HFO-1336mzz(*E/Z*), HFO-1243zf and HFO-1354mzy(*E/Z*).

Furthermore, for HFOs possessing similar substitution patterns containing longer-chain fluorinated groups, analogous reactions are expected to occur, leading to other long-lived F-gases. Figure 1 shows a schematic potential energy surface (PES) for the ozonolysis of HFO-1234ze(*E*) (CHF=CHCF₃), a complex potential energy landscape with a high degree of exothermicity, punctuated by a series of potential energy wells, culminating in CHF₃ and CO₂ formation.

Results

To assess the potential of HFO ozonolysis as a source of long-lived F-gases in the atmosphere, a combination of experiment, theory and global modelling simulations were performed, allowing us to determine product yields, rationalize the underlying chemical mechanisms, and estimate the environmental consequences.

In the experimental phase, several chamber experiments were conducted where CHF₃-yields from the ozonolysis of different HFOs were determined. Experiments consisted of simultaneous high-precision monitoring of HFO consumption and CHF₃ production using the Medusa pre-concentration gas chromatography-mass spectrometry technique(12). To assess atmospheric loss rates of HFOs towards O₃, we determined gas-phase ozonation* rate coefficients for HFO-1234yf, HCFO-1233xf, HFO-1243zf, HFO-1336mzz(*Z*) and HFO-1234ze(*E*) using relative and absolute methods (Figure 2 and *SI Appendix*, Table S2).

The slow ozonation rates exhibited by these HFOs require a large O₃ excess (>100 ppm) to be present in the chamber for long durations – several days for slower reactions, it is therefore imperative that background O₃ losses are exceptionally low such that bimolecular loss through reaction with HFOs remains competitive. The chamber apparatus has been described elsewhere(13–15), with the experimental protocol being adapted to reduce additional O₃ losses, which were minimized by conditioning chamber surfaces with high O₃ concentrations prior to experiments.

Because ozonolysis reactions produce several reactive by-products such as OH and stabilized Criegee intermediates (SCIs), large scavenger concentrations were employed to remove these species. Isopropanol was favored as it reacts rapidly with OH(16) and by analogy to similar systems, will also scavenge SCIs(17–20). Regarding OH, HO₂ is produced from subsequent

* We use “ozonation” here instead of the more commonly used “ozonolysis”. Ozonation is a broader term that can apply to any mechanism of reaction between O₃ and an alkene. Ozonolysis refers strictly to the 1,3-cycloaddition of ozone across an olefinic bond.

reactions with oxygen, but this is not expected to react significantly with haloolefins(21), and will be lost primarily to self-reaction yielding H₂O₂, or reaction with O₃, yielding OH(17). Regarding SCIs, hydroperoxide adducts are expected to form(18), analogous with other systems(22–24). Consistent results were obtained for other scavengers (e.g. combinations of cyclohexane and formic acid).

Of the HFOs studied, three produced quantifiable CHF₃-yields. Figure 2 shows CHF₃-yield data for HFO-1243zf (CH₂=CHCF₃), HFO-1234ze(*E*) (*trans*-CHF=CHCF₃) and HFO-1336mzz(*Z*) (*cis*-CF₃CH=CHCF₃). High linearity, precision and reproducibility between experiments was observed in each case, with similar CHF₃-yields (0.37±0.02 and 0.42±0.02%) exhibited by HFO-1243zf and HFO-1336mzz(*Z*) respectively. Surprisingly, HFO-1234ze(*E*) showed substantially larger yields (3.11±0.05%) than HFO-1336mzz(*Z*) despite it being an asymmetrical alkene with less than unit yield of TFAO. This indicates that the branching of primary ozonide fragmentation is not the primary determinant in CHF₃ production, and that energy partitioning upon cycloreversion and energy transfer of key intermediates play important roles. We also performed experiments upon HFO-1234yf and HCFO-1233xf to investigate possible production of CF₄ and CF₃Cl through analogous reactions. We found no observable production of these long-lived species, nor any CHF₃ production, suggesting that this process is limited to H-migration from the carbon vicinal to the CF₃ group.

To understand this process further, we performed quantum calculations on ozonolysis potential energy surfaces (PES) of three CHF₃-producing HFOs: 1234ze(*E*), 1243zf, and 1336mzz(*Z*) using the ωB97X-D/cc-pVTZ model chemistry(25) implemented in Gaussian 16(26), followed by master equation calculations using MultiWell-2019(27–29), for further details, see *SI Appendix*. Figure 1 provides an overview of CHF₃ production on the PES of HFO-1234ze(*E*) ozonolysis. The reaction proceeds through a van der Waals complex, representing a shallow energy well on the PES, which is not expected to affect the kinetics under tropospheric conditions. Next, a small barrier (~6 kcal mol⁻¹) to forming the primary ozonide (POZ) is encountered. This is a highly exothermic reaction step (~-60 kcal mol⁻¹), and although no collisional stabilization of POZ is predicted, some energy transfer with the bath-gas is anticipated. The POZ undergoes cycloreversion leading to two CIs with a CF₃ substituent: *syn*- and *anti*-TFAO. Qualitatively, trends in CHF₃-yields follow trends in the energies of cycloreversion transition states. The two leading to TFAO are 5–8 kcal mol⁻¹ lower in energy than those leading to CIs with an F substituent (*SI Appendix*, Scheme S1). This corresponds to yields of *syn*- and *anti*-TFAO that are 10 times larger, with simulations predicting a total TFAO yield of 0.906. TFAO will be present in both chemically activated (i.e. “excited”) and stabilized forms, both of which participate in sequential unimolecular reactions, the relative populations of each depending upon bath gas pressure.

Firstly, HFO-1234ze(*E*) ozonolysis is considered. As with all systems described here, the fate of excited TFAO is of primary importance in determining CHF₃-yields, and we begin with this. For both *syn*- and *anti*-TFAO, 1,3-ring closure towards 3-trifluoromethyldioxirane dominates. Analogous to theoretical results of other ozonolysis systems(30–32), we predict that 3-trifluoromethyldioxirane undergoes O–O bond homolysis, forming the bis(oxy) diradical, which decomposes directly via double β-scission to CHF₃ + CO₂, or rearranges in a 1,2-H shift, yielding trifluoroacetic acid (TFA). Some TFA is sufficiently chemically activated (i.e. “hot”) that it decomposes, yielding CHF₃ + CO₂ indirectly through decarboxylation (*SI Appendix*, Schemes S2 and S3). Direct and indirect CHF₃-yields are affected by the barrier heights of these two channels, and also the internal energy of TFA. Master equation simulations show the proportion of indirect to direct CHF₃ production is ~2:1, which is qualitatively consistent with transition states (TS) leading to TFA being ~4 kcal mol⁻¹ lower in energy than corresponding TSs leading directly to CHF₃. The remaining TFAO is present as SCI, either formed “cold” or subsequently stabilized by the bath gas. The pressure dependence of the stabilized *syn*-TFAO yield is shown in Figure 3, where SCI yields increase from ~5–40% from 0–800 Torr. Lower yields (~2–20%) are observed

for *anti*-TFAO, which possesses more internal energy, being formed from a combination of a higher barrier cycloaddition channel and a lower barrier cycloreversion channel than its *syn* counterpart.

Stabilized TFAO is far less efficient at producing CHF₃. Similar to excited TFAO – and excluding bimolecular reactions – 1,3-ring closure towards 3-trifluoromethyldioxirane dominates, with 298K isomerization rates of 5.21×10^{-3} and $1.30 \times 10^{-2} \text{ s}^{-1}$ for *syn*- and *anti*-TFAO respectively. However, depending on reaction rates with various hydrogenous species present in the atmosphere, e.g. H₂O, (H₂O)₂, R(O)OH, ROH, SCIs may be lost towards bimolecular processes, producing various hydroperoxides. In our experiments, [isopropanol] was sufficient to effectively titrate stabilized TFAO, with estimated first-order loss rates of $\sim 5 \times 10^2 \text{ s}^{-1}$, assuming rate coefficients similar to that of CH₂OO with alcohols(18). As with excited CI, upon ring closure, dioxirane is formed. However, 3-trifluoromethyldioxirane may be collisionally stabilized in yields of 61–74% from the *syn*- and *anti*-TFAO respectively at 760 Torr. Homolysis of this stabilized dioxirane becomes negligibly slow ($1.96 \times 10^{-13} \text{ s}^{-1}$), indicating that it is only chemically activated dioxirane that can form CHF₃. The stability of 3-trifluoromethyldioxirane raises the intriguing possibility that ozonolysis results in several novel species which may persist on the timescales of bimolecular reactions. In this regard, fluorinated oxiranes are found to be potent oxidants in laboratory settings, where they efficiently insert into saturated and unsaturated reaction sites(33). The total calculated CHF₃-yield for HFO-1234ze(*E*), 0.636, is shown in SI Appendix, Table S4.

Secondly, HFO-1243zf ozonolysis is considered. Similar to HFO-1234ze(*E*), this reaction forms excited TFAO, which largely controls CHF₃-yields. However, cycloreversion of the primary ozonide formed in HFO-1243zf ozonolysis differs from that in HFO-1234ze(*E*) in two important ways: 1.) The barriers to forming TFAO are now 5–8 kcal mol⁻¹ higher in energy than the barriers to forming CH₂OO, which cannot ultimately form CHF₃. 2.) The transition states leading to TFAO are 12–13 kcal mol⁻¹ higher than the analogous transition states of HFO-1234ze(*E*). According to the statistical rate theory of Forst,(34) this means that the TFAO formed in HFO-1243zf ozonolysis has lower internal energies.. Since CHF₃ production depends on both yields of TFAO and the internal energy with which it is formed, a reduced yield of CHF₃ of 0.022 from HFO-1243zf ozonolysis is anticipated from our calculations.

Thirdly, HFO-1336mzz(*Z*) ozonolysis is considered. The symmetrical structure of this alkene is such that ozonolysis leads to the highest (i.e. unit) yield of TFAO. Since each TFAO formed has the potential to produce CHF₃, intuitively, it might be expected to have correspondingly high yields of CHF₃. However, there are several factors that contribute to this not being the case. 1.) upon formation, the POZ, which is substituted with two CF₃ groups, possesses more heavy atoms and a larger collisional cross section than the other POZs considered here, and is therefore more prone to energy transfer with the bath gas and vibrational relaxation, broadly consistent with previous calculations(35). 2.) energies of the cycloreversion transition states are similar to those encountered in HFO-1243zf (*SI Appendix*, Scheme S5), leading to higher yields of stabilized TFAO (possessing much lower CHF₃-yields). The final calculated yield of CHF₃ is 0.021.

By comparing experimental CHF₃-yields with calculations (see *SI Appendix*, Table S4), we find that although the order of CHF₃-yields is consistent: HFO-1243zf≈HFO-1336mzz(*Z*)<HFO-1234ze(*E*), calculations lead to overestimations of CHF₃-yields. Differences could arise from uncertainties in rates of POZ cycloreversion, for example, underplaying the importance of energy transfer with the bath gas. Other differences could result from not considering reaction channels that compete with ozonolysis, such as epoxidation, which can operate in electron-poor alkenes(36). It appears that vinyl halogen substitutions may be a particularly important consideration in these reactions, which may explain why we see the greatest disparity between calculation and experiment in the case of HFO-1234ze(*E*). Therefore, it may be necessary to perform follow-up experiments to investigate this possibility in HFOs. Nevertheless, as a qualitative indicator of CHF₃ production, these calculations provide insight into the factors that control this yield: the regioselectivity of POZ formation and cycloreversion, which affects yield,

conformation and energy content of the CHF₃-precursor, TFAO; and collisional stabilization of the POZ and TFAO by the bath gas. Furthermore, they confirm our experimental findings, that the “hot acid” channel operates beyond the strictly hydrocarbon systems that have been described previously(7–10).

Discussion

To evaluate the atmospheric implications of these results, the kinetic data of this study were incorporated into global chemistry and transport simulations (see *SI Appendix*), where competitive losses of HFOs towards OH and O₃ were assessed. Wet and dry deposition was neglected in the model, since neither is expected to contribute significantly for this class of compound(37). Furthermore, despite a potentially important influence of temperature and pressure upon collisional stabilization in these reactions, in the absence of quantitative experimental data, we have not included these in our model treatment. Model runs showed that most (~65%) HFO loss by ozonation occurs from 0–3 km, corresponding to 760–530 Torr. Our quantum and master equation calculations suggest that over this pressure range, yields are only mildly and negatively affected by pressure (see Figure 3), which will be offset to some extent by the positive temperature dependence of these reactions (*SI Appendix*, Table S5). In the absence of data, temperature-dependence in the ozone reactions were not included in the model, whose expected positive temperature dependences would increase the fraction lost between 0–3 km and therefore reduce the importance of the pressure dependence of CHF₃ formation.

Figure 4 shows the effects of including ozonolysis upon GWP calculations. For HFO-1234ze(*E*), which has the largest yield of CHF₃ studied, we find that the GWP associated with CHF₃ production is significantly larger than the primary GWP that is calculated based on radiative efficiency and atmospheric lifetime alone. Furthermore, the production of CHF₃ affects these calculations dramatically over longer time-horizons. Whereas the radiative impacts of HFOs are typically not expected to last far beyond their atmospheric lifetimes (~10 days), when ozonolysis products are accounted for, HFO-1234ze(*E*) still has a significant GWP even at the 500-year time horizon.

The fractions of HFOs that are consumed by ozone compared with OH in our global simulations is minor in each case, contributing 2.96%, 1.25% and 0.13% for HFO-1234ze(*E*), HFO-1243zf and HFO-1336mzz(*Z*) respectively. In some circumstances the impact of ozonolysis will be higher than our simulations suggest, since large HFO emissions from the mobile air conditioning sector are expected in some of the world’s most polluted regions(38), where OH can be suppressed by NO_x, leading to O₃/OH ratios that can be higher than global averages(39).

In conclusion, we present experiments and calculations showing that the environmental impact of certain mass-produced HFOs is significantly affected by reactions with O₃. Conventional approaches focus on lifetimes of emitted substances with respect to hydroxyl, the dominant atmospheric oxidant, sparing little attention to reactions with other oxidants and their products. We highlight a pitfall of such a reductionist approach, demonstrating clearly why knowledge of the atmospheric oxidation of molecules should extend beyond their initiation reactions with hydroxyl. Furthermore, we show that precise laboratory work and calculations are absolutely essential if industries are to correctly assess environmental impacts of new chemical products.

Materials and Methods

Details on the chamber experiments, including the measurement of absolute and relative ozonation rate coefficients, CHF₃ product yields, chemical analysis using the Medusa GC/MS technique can be found in *SI Appendix*, Sections 1 and 2. Additional information on computational

methods are provided in SI Appendix, Section 3. A more detailed description of global chemistry and transport modeling, together with GWP calculations is given in SI Appendix, Section 4.

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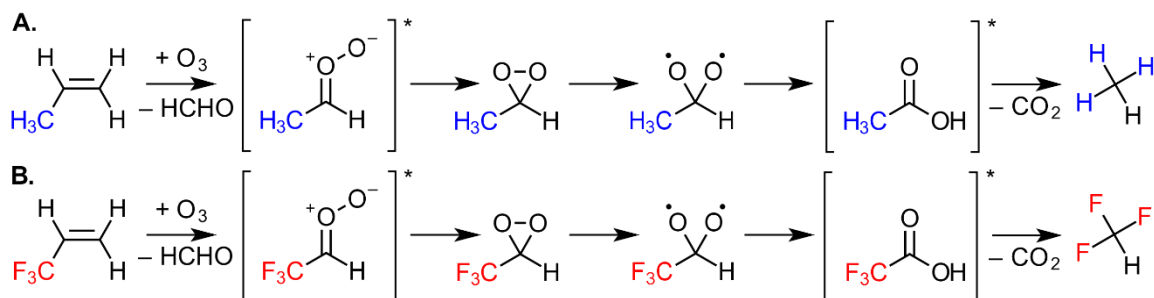
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Figures and Tables



Scheme 1. Reaction sequence A is a simplified representation of the “hot acid” channel in the ozonolysis of propene, resulting in the production of methane from the decarboxylation of acetic acid. Reaction sequence B represents an analogous sequence, whereby CHF₃ is produced from thermally excited trifluoroacetic acid.

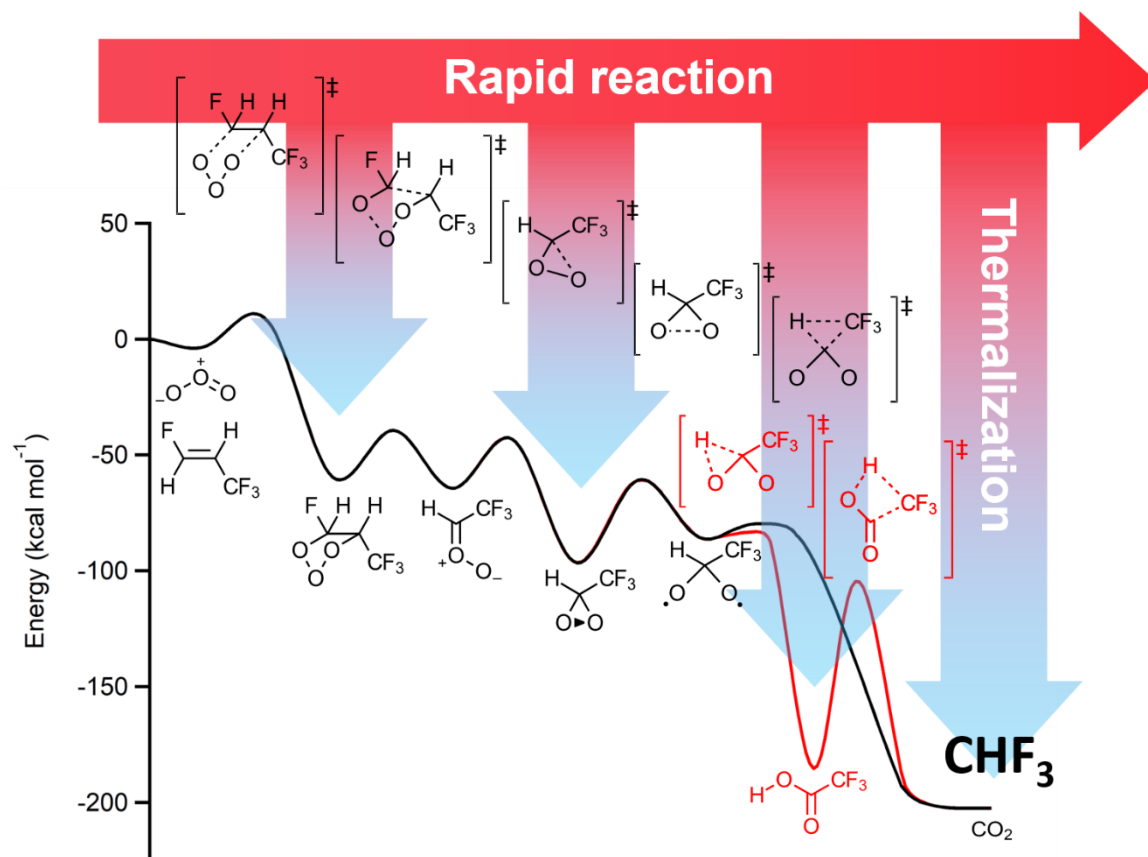


Figure 1. Potential energy surface for the ozonolysis of a popular commercial refrigerant, HFO-1234ze(E). The formation of CHF₃, a potent greenhouse gas, is formed through two energetically favorable reaction channels. The CHF₃-yield is determined by the energy content of key reaction intermediates and the competition between unimolecular rearrangements and collisional deactivation. For simplicity, parallel non-CHF₃-producing channels are not presented.

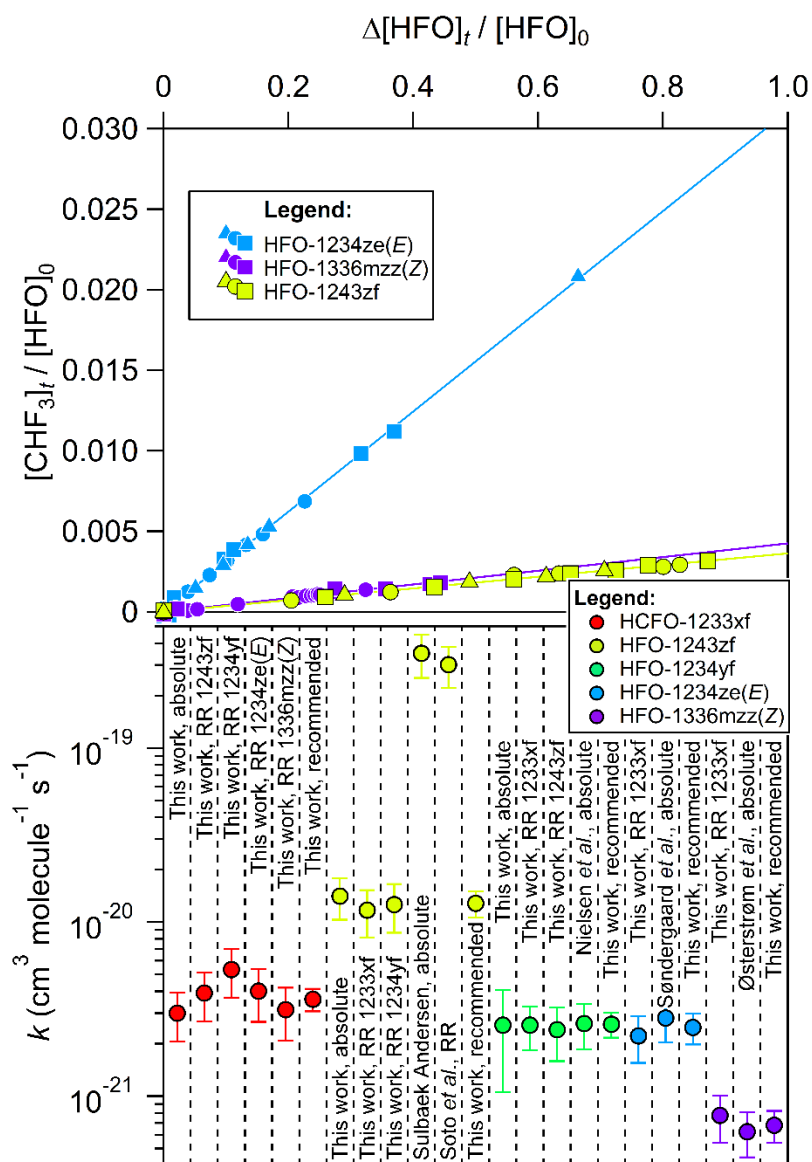


Figure 2. Upper panel: experimentally determined CHF_3 -yields from HFO-1234ze(E), HFO-1243zf and HFO-1336mzz(Z) ozonolysis reactions. Different symbols are used to distinguish separate experiments, demonstrating the precise reproducibility of these data. Lower panel: ozonation rate coefficients of the various haloalkenes considered in this work at 296 K together with available room temperature literature measurements. Excellent consistency is observed between absolute and relative measurements in most cases(40–42), with the exception of two literature values for HFO-1243zf, which are significantly larger than the values reported here(43, 44).

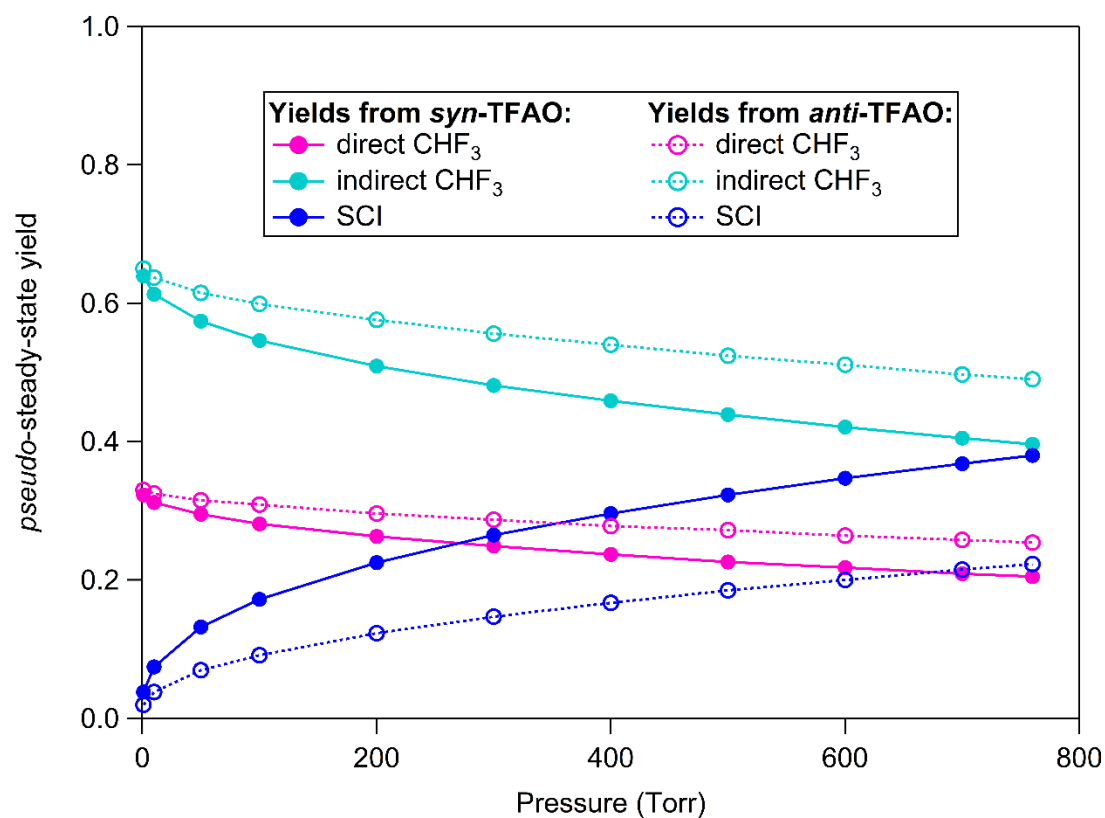


Figure 3. Pressure dependences of the stabilized *syn* and *anti*-TFAO yields in HFO-1234ze(*E*) ozonolysis. Direct and indirect CHF₃ production occurs mainly through excited TFAO unimolecular reactions, therefore, collisional quenching serves to increase the SCI population and decrease the CHF₃-yield.

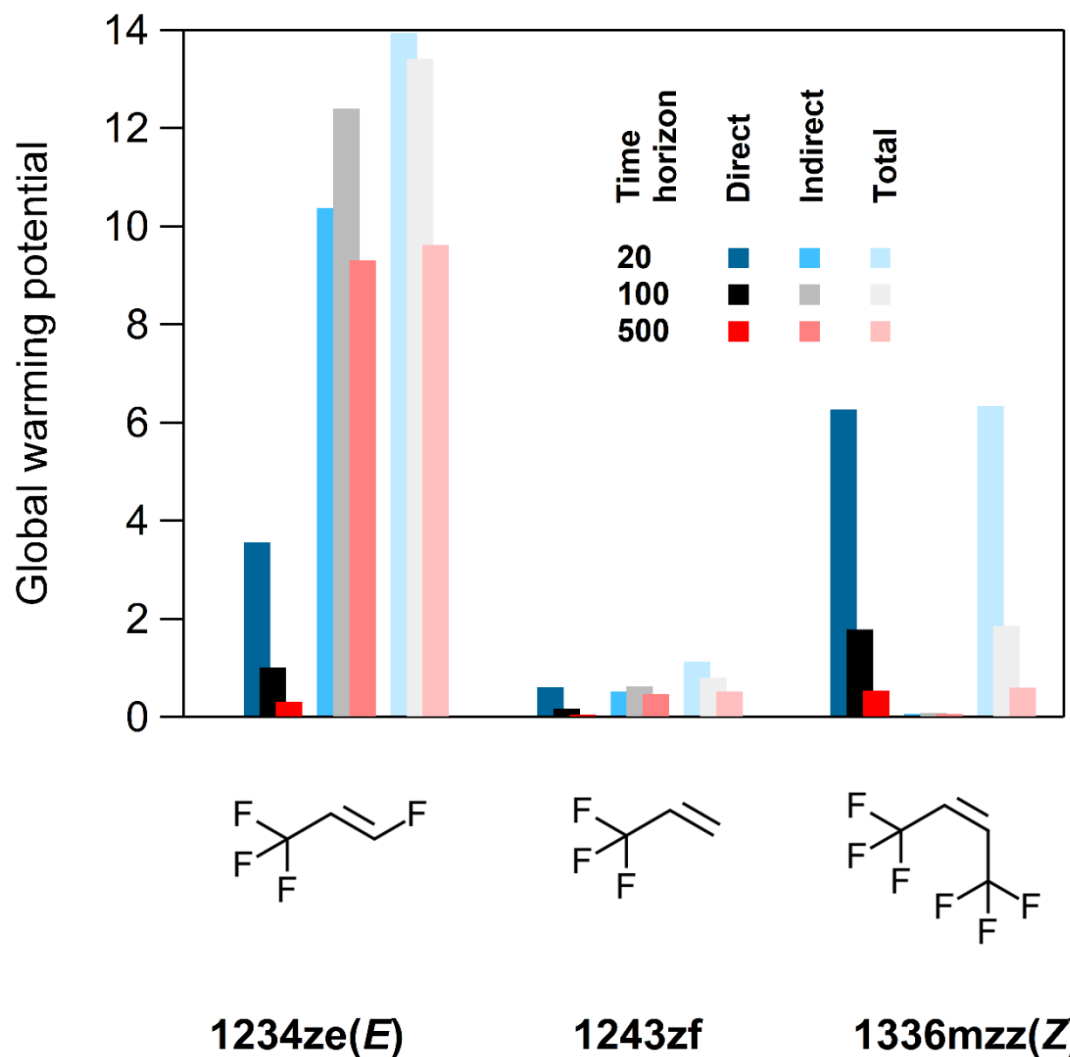


Figure 4. The effects of CHF_3 formation on the calculated global warming potentials of several HFOs considered in this work. The largest effect can be seen for HFO-1234ze(*E*), whose indirect GWP is several times greater than the direct. It can also be seen how its GWP remains virtually unchanged between the 20- and 100-year time horizons and is also non-negligible over the 500-year time horizon, in contrast to current assessments of the environmental impact of this HFO.