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Atmospheric Oxidation of Hydrofluoroolefins and Hydrochlorofluoroolefins by Ozone Produces HFC-23, PFC-14, and CFC-13

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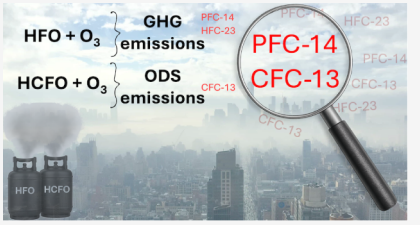
ABSTRACT: Hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) are fluorinated compounds developed to replace refrigerant and propellant gases known to be ozone-depleting substances and/or potent greenhouse gases (GHGs). Their short atmospheric lifetimes result in low direct global warming potentials, but the environmental impacts of their degradation products remain poorly understood. We show that gas-phase ozonolysis of four HFOs produces the long-lived GHGs trifluoromethane (HFC-23) or carbon tetrafluoride (PFC-14), while HCFO-1233xf produces the ozone-depleting chlorotrifluoromethane (CFC-13). At 298 K and 1 bar, the HFC-23 yield is $(7.9^{+0.4}_{-0.2})$% from HFO-1234ze(E) ozonolysis, and the PFC-14 yield is $(1.04^{+0.07}_{-0.05})$% from HFO-1225ye(E), $(1.02^{+0.05}_{-0.05})$% from HFO-1225ye(Z), and $(0.12^{+0.04}_{-0.01})$% from HFO-1234yf, while HCFO-1233xf ozonolysis produces CFC-13 in $(0.034^{+0.009}_{-0.006})$% yield. Global model integrations quantify the atmospheric impacts of these breakdown products. Mechanistic computational studies link the HFO and HCFO molecular structures to the formation of these persistent species, identifying structural features that favor their production. These results highlight the importance of considering not only the direct environmental influence of replacement compounds but also the consequences of their atmospheric degradation. The new insights that emerge will guide efforts to design compounds with lower long-term environmental impacts.



KEYWORDS: *HFO, HCFO, greenhouse gas, global warming potential, ozonolysis*

INTRODUCTION

Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are volatile, fully or partially halogenated alkanes developed for use as inert refrigerants, fire suppressants, solvents, and propellants. Curtailment or cessation of their manufacture for nonfeedstock and dispersive uses in industrialized nations followed recognition of their detrimental environmental impacts: many of these compounds have high global warming potentials (GWPs),[1,2] and those containing chlorine are ozone depleting substances (ODSs), responsible for stratospheric ozone loss, best exemplified by the annual hole in the stratospheric ozone layer over Antarctica.[2] In response to the need for replacements, hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) have emerged as promising alternatives because of their much shorter atmospheric lifetimes.[3] These compounds contain olefinic C═C bonds susceptible to attack by hydroxyl radicals (OH), ozone (O_3), chlorine atoms (Cl) and nitrate radicals (NO_3) in the troposphere. Consequently, HFOs and HCFOs released into the atmosphere have low GWPs and negligible ozone depletion potentials (ODPs). Nevertheless, recent research has focused attention on the products of their atmospheric degradation, identifying long-lived pollutants such as trifluoroacetic acid (TFA), or potent greenhouse gases (GHGs) such as HFC-23, potentially undermining the perceived environmental benefits of replacing HFCs by HFOs in many industrial applications.[4−7]

Most HFOs are removed from the atmosphere by reactions with OH radicals, forming well-established oxidation products such as trifluoroacetaldehyde (CF_3CHO). Although CF_3CHO is photochemically active in the troposphere, recent studies suggest that this photochemistry results in only a small yield of HFC-23 under atmospheric conditions.[8,9] However, other recent findings are raising concerns about the reactive removal of HFOs by ozone; for example, trifluoromethane (CHF_3,

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HFC-23) is a byproduct from the ozonolysis reactions of certain HFOs[4] and HCFO-1233zd.[5] HFC-23 has a GWP of 14700 over a 100-year period, and an atmospheric lifetime of 228 years.[3] HFOs may therefore make an indirect contribution to global warming that will be overlooked if the full pathways and all the products of their atmospheric chemical removal are not carefully considered. The potential risks associated with greater HFO use underline the need for comprehensive environmental assessments of these compounds to ensure that the widespread adoption of this latest generation of halogenated refrigerants and propellants aligns with global climate protection goals. Here, through a combination of laboratory measurements and quantum-chemical calculations, we explore the degradation mechanisms and quantify the yields of GHG and ODS products from ozonolysis of four HFOs and one HCFO. We then model the consequences for atmospheric mixing ratios of these long-lived products, which remain a critical yet poorly understood factor in assessing the atmospheric and climate impacts of HFO use.

MATERIALS AND METHODS

Chamber Measurements of Product Yields from HFO and HCFO Ozonolysis. Ozonolysis reactions were performed at 298 ± 2 K and 1-bar pressure of zero air diluent in a 123-L Teflon-coated stainless-steel chamber (the EXTRA chamber), with chemical analysis of the chamber composition using gas-chromatography and mass spectrometry (GC-MS) methods capable of determining ppt mixing ratios of fluorinated organic compounds. The design and operational details of the EXTRA chamber have been comprehensively described elsewhere.[10]

The ozonolysis of alkenes is known to generate OH radicals with yields ranging from 0.13 to 1.15,[11] which may initiate secondary reactions that compete with the primary reaction between ozone and the compound under investigation.[12] To suppress such interference, an OH radical scavenger was added to the reaction system in the measurements reported here. Isopropanol has been shown to be effective in this role under comparable experimental conditions, and was therefore used in the present study.[4]

Various control experiments were conducted to ensure there were no secondary sources of HFC-23, PFC-14 or CFC-13 from the chamber and associated gas lines and analytical equipment. Commercial zero-air cylinders, used as the primary source of bath gas in this study, are produced through industrial purification processes involving carrier and scrubbing gases, which can introduce background levels of certain compounds. Therefore, background levels of all target compounds, HFO-1234ze(E), HFO-1234yf, HFO-1225ye-(E)/(Z), HCFO-1233xf, HFC-23, PFC-14, and CFC-13 were systematically assessed. PFC-14 and CFC-13 were detected in the zero air, whereas the HFOs, HCFO and HFC-23 were not observed above the detection limit. Particular care was taken to account for background levels of PFC-14, HFC-23 and CFC-13 in the analysis of concentration trends employed in the calculations of product yields (see Section S1 for details).

In the absence of O_3, all reactants were diluted in a zero-air bath and left to mix in the reaction chamber at 298 K and 1 bar pressure for 2−4 days to account for wall losses and possible reaction between the HFO or HCFO (at a mixing ratio of ∼1 ppm) and isopropanol. During this time, the concentration of the HFO or the HCFO remained stable within the experimental measurement uncertainty, and no buildup of HFC-23, PFC-14 or CFC-13 was observed. Similarly, a control experiment using a mixture of O_3 and isopropanol, diluted in zero air, was performed to verify that none of the target products were formed under these conditions. No HFC-23 was detected, and concentrations of PFC-14 and CFC-13 remained at background levels throughout the testing days, consistent with the known impurities in commercial zero-air cylinders. Additionally, as ozone was generated from oxygen supplied by a commercial O_2 cylinder, the potential presence of trace amounts of PFC-14, HFC-23, or CFC-13 in the resulting O_3/O_2 mixture introduced into the EXTRA chamber was carefully considered. Importantly, no measurable increase in PFC-14 or CFC-13 was observed during the investigation of HFC-23 formation from HFO-1234ze(E) ozonolysis. Likewise, no HFC-23 was detected in the ozonolysis experiments of HFO-1225ye(E)/(Z), HFO-1234yf, or HCFO-1233xf, confirming that potential contamination from the O_3/O_2 mixture did not influence the reported product yields.

A rigorous protocol was implemented to clean all the internal surfaces of the chamber before all experimental measurements of HFO and HCFO ozonolysis kinetics and product yields. The cleaning process began by filling the chamber with zero air to a pressure of 1 bar and baking at an elevated temperature for over 20 min, followed by evacuation. Typically, three baking cycles were conducted at temperatures of 40 °C, 60 °C, and 75 °C. The chamber was then held under vacuum as it cooled back to 25 °C. The success of the cleaning process was confirmed by compositional analysis of a zero-air sample in the chamber (at 298 K and 1 bar pressure) using the GC-MS system.

Each experimental quantification of the products formed from an ozonolysis reaction of an HFO or HCFO required a minimum of 2 days and could extend up to 5 days, depending on the initial concentration of the HFO or HCFO and the rate coefficient for its reaction with O_3. Different combinations of the initial HFO or HCFO and O_3 concentrations were tested in the range from 0.2 to 1.2 ppm for the HFO or HCFO, and from 3 to 95 ppm for O_3. To achieve a high fractional completion of the HFO or HCFO ozonolysis, typically reaching above 80% in all experiments, the O_3 concentration was replenished at 4 h intervals. Isopropanol at a mixing ratio of ∼5 ppm was used as an OH scavenger. Table S3 contains detailed information about the experimental conditions.

Ozone was generated *in situ* by a BMT 802X ozone generator, and its concentration inside the chamber was measured by a UV photometric ozone analyzer (Model 427, Rockford) operating at a wavelength of 254 nm. Measurements were made at the start of the reaction, and whenever additional ozone was added to the chamber. To prevent photochemical reactions involving ozone in the analyzer from influencing our measurements of product yields, the ozone monitor was then promptly isolated from the main chamber.

For reaction-product analysis, and to monitor the loss of the reactant HFO or HCFO, the chamber was subsampled using a KNF diaphragm pump (Model number: nXDS6i 100/240v) to pass a small gas sample through a 2 mL loop attached to a 6-port, 2-position valve. The pressure within the loop was monitored using a pressure sensor (DCTi, part number: DC8-P100-L5-1-N11-300-3-111), and an inline needle valve was used to control the back pressure downstream from the loop. Once the loop had been flushed for 1 min with a 160 mL/min flow, the pressure in the loop was recorded and the 2 mL subsample was injected into a Medusa preconcentration unit

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coupled to a gas chromatograph and quadrupole mass spectrometer using 1 L of zero air.

The Medusa GC-MS apparatus has been described in detail before.[13,14] In essence, it combines a preconcentration system with GC-MS separation and analysis to detect sub pmol mol^{-1} amounts of volatile halocarbons such as PFC-14, HFC-23 and CFC-13. For analysis of the EXTRA chamber composition, and to run calibration standards, 2 mL gas samples, diluted to 1 L as described above, were dried using a Nafion dryer with a zero air counter purge and the halogenated organic components were cryogenically trapped at −165 °C on 200 mg Hayesep D at a flow rate of 100 mL min^{-1} to remove O_2 and N_2. The trap was then flash heated to transfer the analytes to a second refocusing trap (containing 5.5 mg Hayesep D) via a molecular sieve 4 Å (150 mg) packed column held at 40 °C to remove any remaining bulk gases, including CO_2. The analytes were then desorbed from the second trap by flash heating to 100 °C and injected into a GasPro PLOT column (60 m long, 0.32 mm i.d.) followed by a PoraBOND-Q PLOT column (25 m long, 0.32 mm i.d.) connected to the mass spectrometer, using He as a carrier gas. The electron ionization quadrupole MS (Agilent 5975) was operated in selective ion mode (SIM) and was cycled through target and qualifier ions for all the compounds of interest during the injection period. Operation in SIM allowed sub-pmol mol^{-1} detection limits. All instrumental control and data processing, including peak identification and integration, used GCWerks.[15]

To minimize the effects of instrumental drift and to calibrate measurement data, calibration standards were analyzed after every second, third or fourth chamber sample. HFC-23 and PFC-14 were calibrated against Scripps Institution of Oceanography derived scales,[16] whereas HFO-1234yf and HFO-1234ze(E) measurements were calibrated against EMPA and METAS derived scales.[17,18] For HFO-1225ye(E)/(Z) isomers and HCFO-1233xf, a primary scale was prepared by sequential manometric dilution of pure compounds (purity information and source: SynQuest Laboratories) using zero air. In the final dilution step, all compounds were spiked into a 34-L stainless steel cylinder, along with 5 mL ultrapure water to help with stability, and pressurized to 32.5 bar, giving mole fractions of (93.8 ± 18.7), (114.2 ± 22.8), (97.9 ± 16.6) pmol mol^{-1} for the HFO-1225ye(E), HFO-1225ye(Z), and HCFO-1233xf, respectively. The reported uncertainties in the standard concentrations account for both instrumental precision and uncertainties associated with the preparation of the concentration standards. Details of these calculations are provided in Section S1.2 and Table S1.

HFO-1234ze(E) (CAS Number: 29118-24-9), HFO-1225ye(E) (CAS Number: 5595-10-8), HFO-1225ye(Z) (CAS Number: 5528-43-8), HFO-1234yf (CAS Number: 754-12-1), and HCFO-1233xf (CAS Number: 2730-62-3) were obtained commercially from SynQuest Laboratories.

The product yield (α) for the ozonolysis of the HFO or HCFO was calculated from the gradient of a graph of the time-dependent product formation ($[Prod]_t$) normalized by the initial HFO or HCFO concentration ($[Prod]_t/[HFO]_0$ or $[Prod]_t/HCFO]_0$) plotted against the fractional change (Δ) in the HFO or HCFO concentration. Yields were determined according to eq 1 (or an analogous equation for the HCFO):

$$[Prod]_t/[HFO]_0 = \alpha(\Delta[HFO]_t/[HFO]_0) \quad (1)$$

Computational Methods. The initial steps of the reaction of O_3 with selected HFOs were characterized using density functional theory. Specifically, the ωB97X-D density functional and the cc-pVTZ basis set were used to compute electronic energies, optimized geometries, and harmonic vibrational frequencies for the reactants, intermediates, transition states, and products. The relative energies reported here are at 0 K, where the zero-point vibrational energies were based on harmonic frequencies scaled by 0.975. The calculations were performed using Gaussian 16.[19]

Modeling of the atmospheric impacts of HFO ozonolysis used STOCHEM-CRI, a 3D tropospheric chemical transport model. This model operates such that chemistry and transport processes are uncoupled (allowing timesteps to be determined locally) and is driven by archived meteorological data from the UK Meteorological Office (Met Office).[20] The "offline" model functions at the atmospheric resolution of the Met Office unified model (1.25° longitude × 0.83° latitude × 12 uneven vertical levels). The data outputs include: pressure, temperature, humidity, interpolated wind data, tropopause height, cloud amount, precipitation, boundary layer height, and surface parameters. The meteorological module of STOCHEM has been discussed in detail previously,[20] and updates can be found in Derwent et al.[21] The chemical mechanism used in STOCHEM is the Common Representative Intermediates (CRI) version 2 reduction 5 (CRI v2-R5). CRI v2-R5 was developed initially by Jenkin et al.[22] from the Master Chemical Mechanism (https://mcm.york.ac.uk/MCM/) with subsequent improvement by Watson et al.[23] More details of the CRI v2-R5 mechanism can be found in Utembe et al.[24,25] and recent updates of the CRI v2.2 mechanism are described by Jenkin et al.[26]

Emissions are treated as an additional term to the chemical production of each species during each integration time step.[20,27] The emission profile for STOCHEM-CRI consists of three different categories: surface emissions, stratospheric sources and 3-dimensional emissions. Surface emissions are anthropogenic, and from biomass burning, oceans, soils and vegetation; these are mapped monthly from a two-dimensional source map at a resolution of 5° longitude × 5° latitude. The emissions data employed in the base case STOCHEM-CRI model were adapted from the Precursors of Ozone and their Effects in the Troposphere (POET) inventory for the year 1998.[28] The emissions flux is implemented during the chemical time step unless there are no Lagrangian cells present in a particular Eulerian grid cell, in which case the emissions are stored for implementation after the next advection step. Finally, all emissions are converted into units of molecule per second per grid square.

In the current study, HFO-1234yf, HFO-1225ye(E), HFO-1225ye(Z), HFO1234ze(E) and HCFO1233xf were added to STOCHEM-CRI. Each HFO/HCFO was emitted at a rate of 0.042 Tg yr^{-1} (each taken as 1/5 of the total estimated HFC-134a emission of 0.21 Tg yr^{-1} from the 2015 BEIS report to give a "full-transition" scenario where only these 5 HFO/HCFO compounds are used) and loss processes included reaction with OH and O_3. For HFC-23, PFC-14 and CFC-13, emissions were set to 0 such that all occurrences of these chemicals in the modeled atmosphere were a result of HFO/HCFO degradation, and the only losses included were those resulting from reactions with OH and $O(^1D)$. More details can be found in the SI (Section S2).

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RESULTS AND DISCUSSION

Our comprehensive approach to evaluate the potential environmental impact of ozonolysis products from four HFOs and one HCFO combines experimental measurements of the evolving chemical composition within a simulation chamber containing low mixing ratios of the target HFO or HCFO and ozone, theoretical elucidation of reaction pathways via calculations, and global atmospheric chemistry and transport modeling. The compounds studied are HFO-1234ze(E) (trans-1,3,3,3,3-tetrafluoropropene; trans-$CF_3CH{=}CHF$), HFO-1234yf (2,3,3,3,3-tetrafluoropropene; $CF_3CF{=}CH_2$), HFO-1225ye(E) ((*E*)-1,2,3,3,3-pentafluoropropene; (*E*)-$CF_3CF{=}CHF$), HFO-1225ye(Z) ((*Z*)-1,2,3,3,3-pentafluoropropene; (*Z*)-$CF_3CF{=}CHF$), and HCFO-1233xf (2-chloro-3,3,3-trifluoropropene; $CF_3CCl{=}CH_2$).

Table 1 compiles the product yields determined by GC-MS analysis for all the ozonolysis reactions investigated in this study and reports the corresponding average values. A more detailed version of this table is provided in the Supporting Information (Section S1, Table S3), which also lists the initial experimental concentrations and the specific conditions under which each measurement was performed. The uncertainties associated with the yields reported in Table 1 include all contributions, encompassing both instrumental precision and the propagation of errors arising from the quantification and calibration procedures. Full details are provided in Section S1.2.

Experimental investigations of the ozonolysis of the selected HFOs and HCFO reveal that both the number and the arrangement of fluorine atom substituents in the molecular structure significantly influence the reaction mechanisms and product yields. When HFO-1234ze(E) reacts with ozone at ambient temperature (298 K) and pressure (1 bar of zero air), it produces HFC-23 with a yield of $(7.9^{+0.4}_{-0.2})$%, (Figure 1). This HFC-23 formation requires an H atom substituent on the olefinic C atom bonded to the CF_3 group. Substitution of this hydrogen by a fluorine atom instead favors the formation of carbon tetrafluoride (CF_4; PFC-14). This latter pathway is exemplified by the ozonolysis of HFO-1225ye, where both the E and Z isomers produce measurable amounts of PFC-14, with yields of $(1.04^{+0.07}_{-0.05})$% and $(1.02^{+0.05}_{-0.05})$%, respectively (Figure 1). In comparison, HFO-1234yf exhibits a lower yield of PFC-14, with an upper limit of $(0.12^{+0.04}_{-0.01})$% (Figure 1). These different outcomes highlight how an additional fluorine substituent enhances PFC-14 formation, for reasons that are discussed below. Despite the nominal CF_4 yield of 0.12%, this result remains environmentally relevant as HFO-1234yf is increasingly used to replace HFCs.[3] The first long-term atmospheric record of HFO-1234yf was recently reported[29] and reveals a marked increase in its abundance, from approximately 0.03 ppt in the mid-2010s to about 0.25 ppt in 2024, and a corresponding rise in northwest European emissions from 0.03 to 1.50 Gg yr^{-1} over the same period. These observations demonstrate the accelerating introduction of HFO-1234yf into the atmosphere and highlight the potential environmental significance of even minor formation of PFC-14 from its atmospheric degradation, which could lead to cumulative environmental impacts.

The observations described above support the previously proposed mechanism for HFC-23 or PFC-14 production through Criegee intermediates that can isomerize and eliminate these products either directly or via internally excited ("hot") TFA molecules.[4] To test this proposed mechanism further, we measured PFC-14 yields from HFO-1225ye(Z) at pressures of 1−3 bar of zero air. With an increase in bath-gas pressure, the PFC-14 yields fell from 0.97% (1 bar) to 0.81% (2 bar) and 0.66% (3 bar), consistent with greater collisional stabilization of internally hot TFA molecules suppressing the thermal decomposition to PFC-14 over an activation barrier (SI Section S3).

For the reaction between HCFO-1233xf and O_3, low levels of chlorotrifluoromethane (CF_3Cl; CFC-13) were observed, with a yield of $(0.034^{+0.009}_{-0.006})$%. Although small, this finding exposes the potential impact of widespread use of this HCFO on the stratospheric ozone layer because CF_3Cl is a known ODS, with an ODP of 0.3 and an atmospheric lifetime of 640 years.[1,3] Concerns about the use of this HCFO are further

Table 1. Experimental Yields (α_i for Replicate Measurement) for Fluorinated Products Identified from the Ozonolysis of HFOs and HCFOs, along with Their Corresponding Average Values

HFO	Product Identified	Yield[a]
HFO-1234ze(E)	HFC-23	$\alpha_1 = (0.075^{+0.006}_{-0.003})$
		$\alpha_2 = (0.080^{+0.006}_{-0.002})$
		$\alpha_3 = (0.0792^{+0.002}_{-0.0007})$
		$\alpha_4 = (0.080^{+0.006}_{-0.002})$
		$\alpha_5 = (0.0833^{+0.001}_{-0.0006})$
		Yield = $(0.079^{+0.004}_{-0.002})$[b]
HFO-1225ye(E)	PFC-14	$\alpha_1 = (0.011^{+0.0005}_{-0.001})$
		$\alpha_2 = (0.0098^{+0.0003}_{-0.0009})$
		$\alpha_3 = (0.010^{+0.0004}_{-0.001})$
		$\alpha_4 = (0.0103^{+0.0002}_{-0.0001})$
		$\alpha_5 = (0.01082^{+0.0009}_{-0.0002})$
		Yield = $(0.0104^{+0.0007}_{-0.0005})$
HFO-1225ye(Z)	PFC-14	$\alpha_1 = (0.0097^{+0.0007}_{-0.0005})$
		$\alpha_2 = (0.0100^{+0.0004}_{-0.0009})$
		$\alpha_3 = (0.0108^{+0.0007}_{-0.0004})$
		$\alpha_4 = (0.0103^{+0.0004}_{-0.0002})$
		Yield = $(0.0102^{+0.0005}_{-0.0005})$
HFO-1234yf	PFC-14	$\alpha_1 = (0.0012^{+0.0008}_{-0.0002})$
		$\alpha_2 = (0.0010^{+0.00009}_{-0.00004})$
		$\alpha_3 = (0.0016^{+0.0003}_{-0.0001})$
		Yield = $(0.0012^{+0.0004}_{-0.0001})$
HCFO-1233xf	CFC-13	$\alpha_1 = (0.00034^{+0.0001}_{-0.00002})$
		$\alpha_2 = (0.00034^{+0.00006}_{-0.00007})$
		$\alpha_3 = (0.00033^{+0.00006}_{-0.00008})$
		Yield = $(0.00034^{+0.00009}_{-0.00006})$

[a]Uncertainties include all contributions discussed in Section S1.2. [b]The average yield of HFC-23 reported here is higher than the previously reported value, (3.11 ± 0.05)% for HFO-1234ze(E).[4] This difference is further discussed in the main text.

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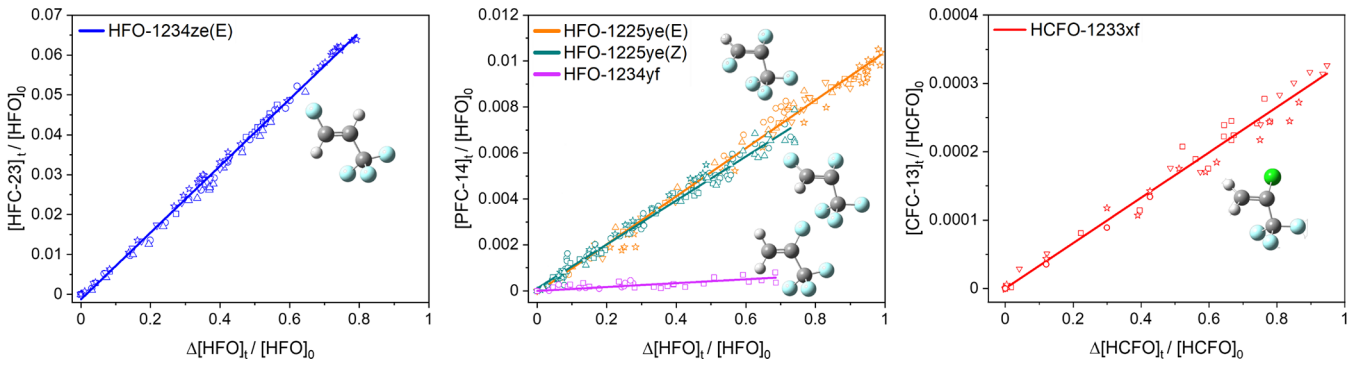

Figure 1. Experimentally determined product yields from HFO and HCFO ozonolysis at 298 K and 1 bar pressure in zero air: Left panel: HFC-23 from HFO-1234ze(E) (blue); Middle panel: PFC-14 from HFO-1225ye(E) (orange), HFO-1225ye(Z) (teal), and HFO-1234yf (lilac); Right panel: CFC-13 from HFCO-1233xf (red). Different symbols distinguish separate experiments. The panels show the ratio of products to initial HFO or HCFO concentrations plotted against the fractional change in the HFO or HCFO concentration. A detailed list of the product yield measurements is available in SI Section S1.

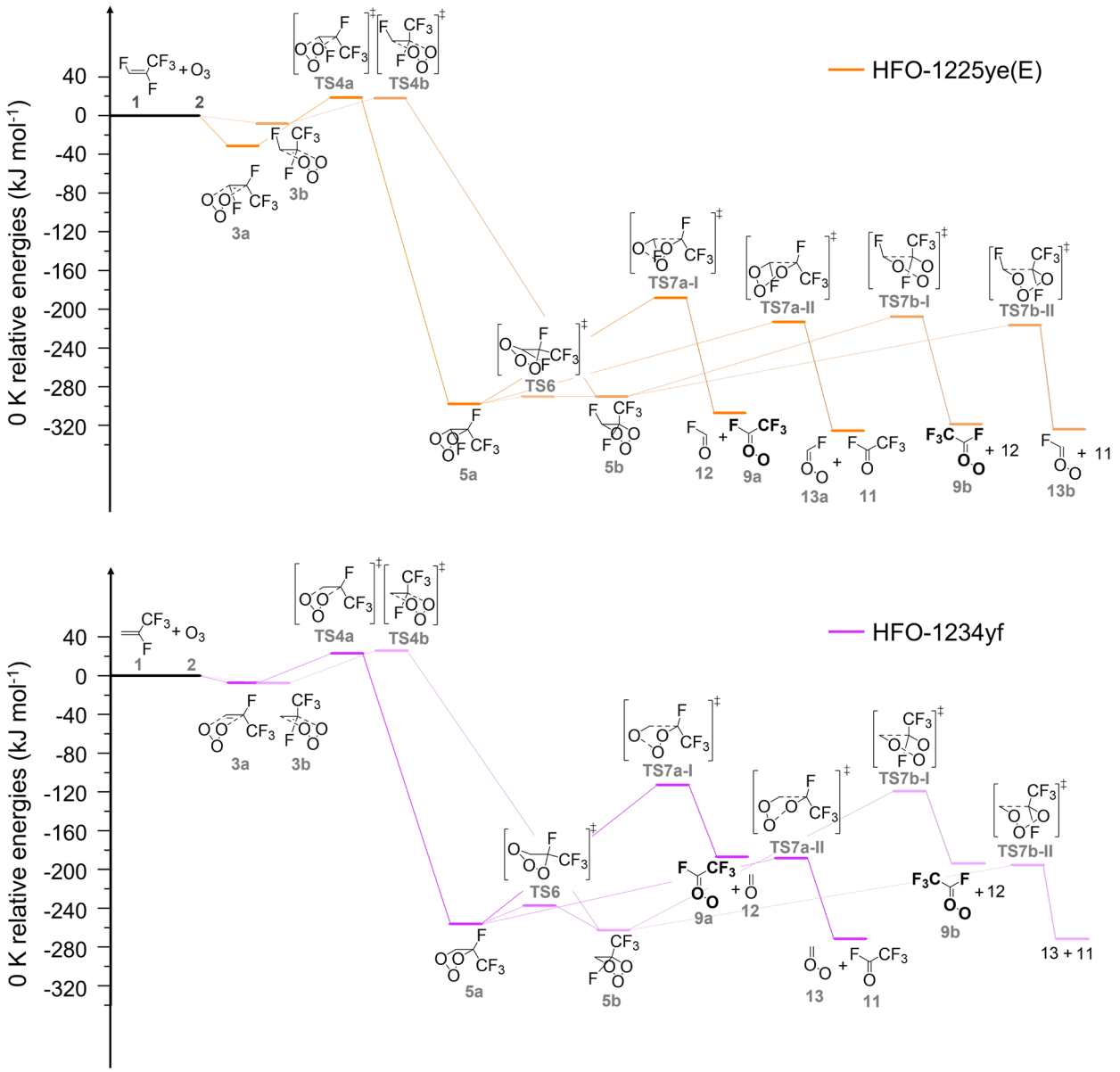

Figure 2. Computed relative energies for the intermediates and transition states involved in the first steps of the ozonolysis of HFO-1225ye(E) (top panel) and HFO-1234yf (bottom panel). Labels indicate related species arising from the different reaction pathways of each HFO.

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magnified by its significant industrial demand, as an intermediate in the production of HFO-1234yf,[30−34] which is widely used in automotive air-conditioning systems. The use of HCFO-1233xf in HFO-1234yf production suggests that substantial amounts of this HCFO could have already been released into the troposphere.

Our experimentally determined yields for HFC-23 are higher than a previously reported value of (3.11 ± 0.05) % for HFO-1234ze(E) obtained using the same experimental apparatus.[4] Possible secondary sources of the quantified product were excluded by systematically characterizing the components of our experimental setup and careful control experiments (see the Materials and Methods section for details). We attribute the greater yields now reported to refinements to the experimental procedure to ensure higher (up to 80%) fractional consumption of the HFO by ozonolysis in the reaction chamber, and more frequent use of calibration standards during the GC-MS measurements. Recent atmospheric observations of HFO-1234ze(E) point to the environmental relevance of these findings, showing an increase in midwinter baseline abundances from around 0.03 ppt in the mid-2010s to approximately 0.25 ppt in 2024, and observation-based emission estimates for northwest Europe reaching 0.96 Gg yr^{-1} in 2023.[29] Collectively, these results indicate that the environmental impact of the ozonolysis reaction of HFO-1234ze(E) will therefore be greater than previous modeling suggested.[4] These consequences are explored further below.

PFC-14 is recognized to be one of the most potent and longest-lived GHGs, and is regulated by the Paris Agreement (and formerly the Kyoto Protocol) to the United Nations Framework Convention on Climate Change. It is the most abundant perfluorocarbon (PFC) in the atmosphere, with a lifetime of at least 50,000 years and a GWP of 7490 (100-year horizon).[35−41] Our experimental measurements show that PFC-14 is a product of the ozonolysis reactions of HFO-1225ye(E)/(Z) and HFO-1234yf, with yields from HFO-1225ye(E)/(Z) close to 1% under ambient conditions of pressure (1 bar) and temperature (298 K). In contrast, the PFC-14 yield from ozonolysis of HFO-1234yf under identical conditions is 0.1% or less.

To provide further insight into the reaction mechanism producing CF_4, and factors controlling the yield, we employed quantum-chemical calculations to characterize key features on the potential energy surfaces (PES) associated with the ozonolysis of these three HFOs. Figure 2 compares the potential energies of key reaction intermediates for the exothermic formation of primary ozonides (POZs) from the addition of ozone to two of the three HFOs, and for the transition states for the cycloreversion decomposition of the POZs into carbonyl compounds and Criegee intermediates. The pathway posited to form CF_4 is decomposition of the Criegee intermediate CF_3CFOO (structures 9a and 9b, Figure 2), which is likely to form with considerable internal energy, as suggested by the calculated profiles in Figure 2.[42,43] Relative to the separated HFO-1234yf and O_3 reactants (Figure 2 and Scheme S1), the barriers for cycloreversion from the POZ to CF_3CFOO are submerged, but they are ∼80 kJ mol^{-1} higher than the barrier to the alternative Criegee intermediate, CH_2OO, suggesting that the CF_3CFOO pathway will be negligible. This analysis is consistent with the 0.12% yield of CF_4 from HFO-1234yf ozonolysis in our experimental measurements. In contrast, for the POZs formed by addition of ozone to both *E* and *Z* isomers of HFO-1225ye, the submerged cycloreversion barriers leading to either CF_3CFOO or FCHOO Criegee intermediates differ by only ∼20 kJ mol^{-1}. Relative to the reactants, the formation of the Criegee intermediates is more exothermic for the HFO-1225ye *E* and *Z* isomers than for HFO-1234yf, providing greater internal energy for further isomerization or decomposition. For both these reasons, the pathway to CF_3CFOO, with subsequent decomposition to PFC-14, becomes more competitive for the HFO-1225ye isomers, consistent with our higher (1%) measured yields. A more detailed depiction of the mechanism can be found in SI Section S4.

The results of this analysis highlight two structural features that may influence the formation of persistent fluorinated byproducts. First, placement of a hydrogen or fluorine atom on the same carbon of the C═C bond as the CF_3 group promotes pathways leading to HFC-23 or PFC-14 formation, respectively. Second, for the latter, the presence of a second fluorine atom bonded to the other olefinic C atom encourages the formation of CF_3CFOO Criegee intermediates, which can decompose into long-lived fluorinated products. Third, TFA will form if there is a $-CF_3$ group attached directly to one of the olefinic carbon atoms, and its yield is determined by the nature of the substituent on the same carbon. These observations offer a framework to guide HFO molecular designs that reduce yields of atmospherically persistent and damaging products of their oxidation chemistry.

In the troposphere, the primary removal pathways for HFOs and HCFOs are reactions with atmospheric oxidants, most importantly hydroxyl radicals and ozone, while solar photolytic degradation plays a negligible role. Despite O_3 being far more abundant than OH in the troposphere, the much larger rate coefficients for reactions of HFOs with OH than O_3 ($k_{OH} \gg k_{O3}$) render the OH-reaction pathway the dominant atmospheric sink. The consequences of these oxidation reactions for atmospheric HFC-23 and PFC-14 mixing ratios can be quantified using atmospheric chemistry and transport models. Here, selected HFOs and HCFOs, with literature-derived OH-initiated oxidation rate coefficients, laboratory measured ozonolysis rate coefficients, and new product yields, were incorporated into the global chemical transport model STOCHEM-CRI to evaluate their atmospheric fates and environmental impacts. Ozonolysis rate coefficients were determined experimentally in this study for HFO-1234ze(E), HFO-1225ye(Z), and HFO-1225ye(E) under controlled laboratory conditions (see Supporting Information, Section S2.1). The derived bimolecular rate coefficients were (2.79 ± 0.12) × 10^{-21}, (1.97 ± 0.34) × 10^{-21}, and (2.00 ± 0.18) × 10^{-20} cm^3 $molecule^{-1}$ s^{-1}, respectively, showing good agreement with the previously reported values of (2.81 ± 0.12) × 10^{-21}[3,44] (1.45 ± 0.15) × 10^{-21}[45], and (1.98 ± 0.15) × 10^{-20} cm^3 $molecule^{-1}$ s^{-1}.[45] In addition, emission values of 0.042 Tg yr^{-1} were assigned to each of the included HFO/HCFOs to represent an evenly split, total replacement scenario for the 0.15 Tg yr^{-1} emission value reported for HFC-134a.[46]

Ozonolysis contributed <1% to the atmospheric removal of all HFO and HCFO compounds studied, with only a small fraction of this loss pathway leading to HFC-23, PFC-14, or CFC-13. Nevertheless, over a 10-year time scale, the cumulative additional atmospheric burdens of these byproducts are projected to be 104.4, 45.3, and 1.0 tonnes, respectively. When compared to current emission levels,[3] these contributions represent a relatively minor fraction (<1% in each case). However, under future scenarios characterized by

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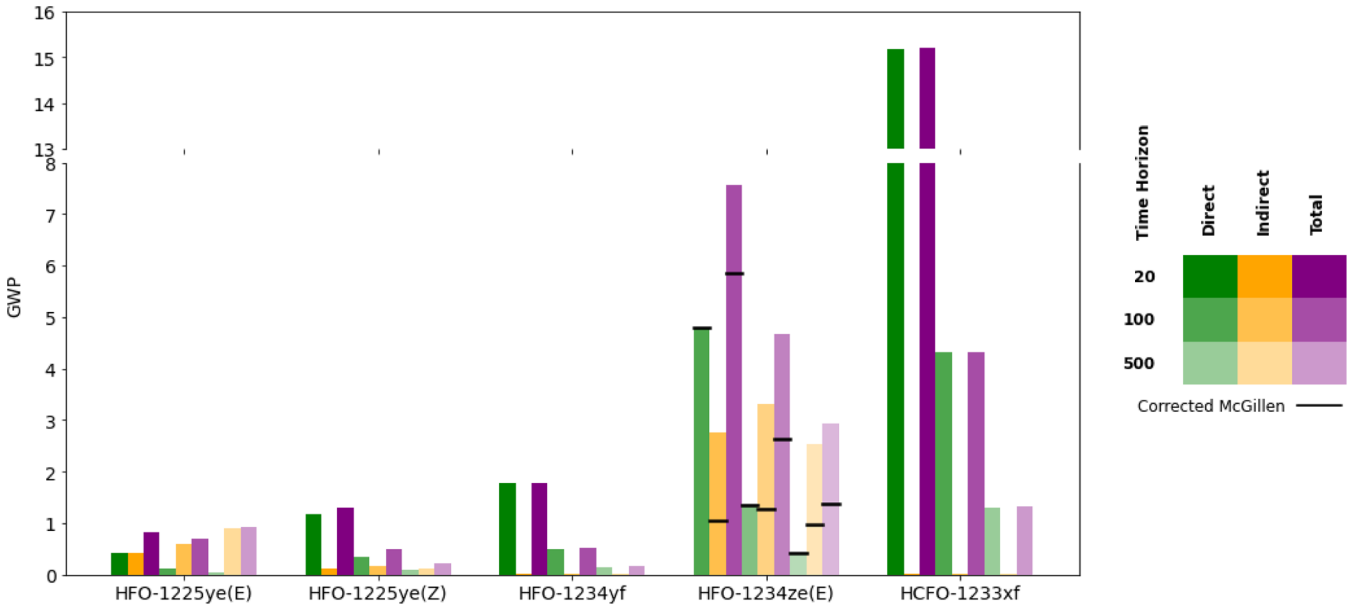

Figure 3. Contributions of PFC-14, CFC-13, and HFC-23 formation to the GWP of the HFOs and HCFOs investigated in this study. The black horizontal markers over the HFO-1234ze(E) data correspond to updated values using product yields from McGillen et al.[4] with revised GWP calculations.

reduced direct emissions of long-lived greenhouse gases and consequent greater use of the studied HFOs/HCFOs, the contribution from product GHG and ODS forming pathways will become more significant.

We have updated and expanded previous work[4] by calculating the indirect GWPs associated with ozonolysis, based on the new product yields reported here. Figure 3 compares these indirect values with direct GWPs derived from radiative efficiencies and atmospheric lifetimes.

The indirect GWPs associated with PFC-14 production from HFO-1225ye(E) and HFO-1225ye(Z) ozonolysis are significantly different despite their similar product yields. The indirect contribution to GWP is elevated for HFO-1225ye(E) (~0.4) compared with its isomer because of the factor of 10 difference in their reaction rate coefficients with ozone. The indirect GWP of HFO-1234yf (also associated with PFC-14 production) is closer to that of HFO-1225ye(Z). Both remain low, even at the 500-year time horizon, with values ranging from 0.03 to 0.12.

A previous publication from our laboratory reported that the GWP associated with HFC-23 formation from HFO-1234ze(E) was significantly higher than the direct GWP of this HFO.[4] However, corrected model calculations give an indirect GWP approximately ten times lower than previously reported (1.1 versus ~10.0[4] at the 20-year time horizon), along with a slightly higher direct GWP (~4.8 versus ~3.8[4]). Corrected GWPs are shown by black horizontal lines in Figure 3. As a result of the greater HFC-23 yield from HFO-1234ze(E) ozonolysis obtained in the current study compared to prior work, the indirect GWP is enhanced to 2.8, with similar enhancements observed at the 100-year (3.3) and 500-year (2.5) time horizons.

While the direct climate impact of greater use of HFOs and HCFOs remains low because of their short atmospheric lifetimes, minor products of their gas-phase ozonolysis have high global warming potentials and, in some cases, ozone-depletion potentials. Although current contributions from these secondary products appear limited in magnitude, their persistence and cumulative effects warrant consideration, particularly under scenarios of increasing global use of HFOs and HCFOs. These findings suggest that assessments of the use of these halogenated alternatives to CFCs and HFCs should systematically account for indirect environmental impacts arising from their atmospheric degradation. Such assessments could support ongoing efforts to refine compound selection and risk-evaluation frameworks under international climate and ozone agreements. From an industrial perspective, our study highlights the value of incorporating atmospheric degradation profiles into the early stage development and screening of next-generation fluorinated compounds, to ensure long-term environmental compatibility alongside performance requirements. To guide industrial development of future HFOs and HCFOs, we have identified structural motifs that promote the formation of undesirable GHG and ODS products of their atmospheric oxidation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.5c11383.

PFC-14 and CFC-13 background concentrations and growth during ozonolysis of HFO-1225ye(E) and HCFO-1233xf; product yields, kinetic measurements, and analysis for O_3 + HFO reactions at 298 K; chamber pressure effects on PFC-14 yields from ozonolysis of HFO-1225ye(Z); calibration scales, standards, error analysis, and propagated errors; kinetic data used in STOCHEM-CRI for atmospheric modeling of HFO/HCFO chemistry and the GHG products; relative energies (0 K, kJ mol^{-1}) of intermediates and transition states for initial ozonolysis steps of HFO-1234yf and HFO-1225ye(E)/(Z) from ωB97X-D/cc-pVTZ calculations (PDF)

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Notes

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ABBREVIATIONS

CFC	chlorofluorocarbon
CFC-13	chlorotrifluoromethane
GHG	greenhouse gas
HCFO-1233xf	2-chloro-3,3,3-trifluoroprop-1-ene
HFC	hydrofluorocarbon
HFC-23	trifluoromethane
HFO	hydrofluoroolefin
HFO-1225ye(E)	(*E*)-1,2,3,3,3-pentafluoro-1-propene
HFO-1225ye(Z)	(*Z*)-1,2,3,3,3-pentafluoro-1-propene
HFO-1234yf	2,3,3,3-tetrafluoropropene
HFO-1234ze(E)	trans-1,3,3,3-tetrafluoroprop-1-ene
ODS	ozone depleting substance
PES	potential energy surface
PFC-14	carbon tetrafluoride
POET	Precursors of Ozone and their Effects in the Troposphere
POZ	primary ozonide

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