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

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Photodissociation of CF_3CHO provides a new source of CHF_3 (HFC-23) in the atmosphere: implications for new refrigerants.

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Summary paragraph

Throughout the last century, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) were the most widely used refrigerants. However, it was discovered that they released reactive chlorine in the upper atmosphere causing the hole in the ozone layer and they were phased out by the 1987 Montreal Protocol [1]. They were replaced by hydrofluorocarbons (HFCs), which contain no chlorine and do not damage the ozone layer. However, HFCs are potent greenhouse gases and they were phased out in a 2016 amendment to the Montreal Protocol [2]. The latest evolution of these refrigerants is the hydrofluoroolefins (HFOs). These molecules have no chlorine and incorporate a carbon-carbon double bond to greatly reduce their atmospheric lifetime, and hence their contribution as a greenhouse gas. In this work, we demonstrate that one of the most important HFOs in current use ultimately decomposes partially into HFC-23 (CHF_3) in the atmosphere. HFC-23 is one of the most potent greenhouse gases known, and the most potent HFC. Despite its phaseout, the observed emissions of HFC-23 have been increasing recently and were the largest in history in 2018 with no conclusive explanation [3]. This work suggests that the production of HFOs might be partially responsible.

Main text

Halogenated molecules were widely used as refrigerants, propellants, foam blowing agents, fire retardants and other useful chemicals throughout the last century. The chlorofluorocarbons (CFCs) were, by far, the most proliferated until it was realised that their emission was contributing reactive chlorine to the upper atmosphere and causing the hole in the ozone layer. This led to the 1987 Montreal Protocol [1] that governed the global phasedown of CFCs via the hydrochlorofluorocarbons (HCFCs) as interim replacements that still deplete ozone, but to a much lesser extent. Ultimately, CFCs and HCFCs were replaced by hydrofluorocarbons (HFCs), which contain no chlorine and have no ozone depletion potential (ODP). However, HFCs are long-lived and potent greenhouse gases. Global warming potentials (GWPs) are used to compare newly-emitted greenhouse gases according to their contribution to surface heating, typically over 100 years and relative (by mass) to carbon dioxide *i.e.* $\text{GWP}(\text{CO}_2) = 1$. Typical HFCs exhibit GWPs in the thousands and up to 12 690 in the case of fluoroform (CHF_3 or HFC-23) *e.g.* 1 tonne of fluoroform, emitted today, contributes as much to surface heating over 100 years as 12 690 tonnes of CO_2 . Concerns about offsetting the hard-won environmental gains brought about by the CFC and HCFC phasedown led to the addition of HFCs in the 2016 Kigali amendment to the Montreal Protocol [2].

The leading replacement candidates are a new class of compounds called hydrofluoroolefins (HFOs), which have already been emitted and detected in the atmosphere in significant quantities [4]. These compounds are derived from HFCs but incorporate a carbon-carbon double bond that increases their reactivity, leading to much shorter atmospheric lifetimes (weeks compared to decades/centuries) and near-zero GWPs. One

important HFO, currently, is HFO-1234ze ($\text{CHF}=\text{CH}-\text{CF}_3$) with zero ODP and a GWP < 1 (*i.e.* less than CO_2) [5]. These GWP estimates rely on chemical knowledge concerning the decomposition of the HFO and of its onward degradation products. It is known that atmospheric decomposition of HFO-1234ze yields trifluoroacetaldehyde (CF_3CHO) with 100% molar yield [6], which is then removed from the atmosphere $4\times$ faster than its progenitor via photolysis [7]. Studies dating back to the 1950s suggest that photolysis leads to trifluoromethyl (CF_3) and formyl (CHO) radicals [8–10] that lead to atmospherically less hazardous CO_2 and HF [6].

The apparently simple photochemistry of CF_3CHO is in contrast to similar carbonyl species. Acetaldehyde (CH_3CHO), the non-fluorinated analogue of CF_3CHO , is known to exhibit far more complex photochemistry than reported for CF_3CHO with multiple decomposition product channels. Analogous to CF_3CHO , the dominant photolysis pathway for CH_3CHO at all tropospherically-important wavelengths yields CH_3 and CHO radicals [11–14]. However, following absorption of an ultraviolet photon, CH_3CHO can also access a rich photochemistry on the ground electronic state (S_0). These many ground state photodissociation pathways are discussed in the following section and, most importantly, include the exoergic formation of methane (CH_4) and carbon monoxide (CO) [15–17]. Fluoroform (CHF_3 or HFC-23) is the product analogue of CH_4 for CF_3CHO . This is concerning as HFC-23 is the most environmentally hazardous HFC with a GWP of 12 690 [5].

In this paper, we demonstrate that CF_3CHO photolyses to form HFC-23. Although the quantum yield is small, this pathway could account for the fate of $11.0 \pm 5.5\%$ of atmospheric CF_3CHO . This will considerably increase the ‘effective GWP’ of any HFO that includes CF_3CHO in its decomposition scheme.

Photodissociation pathways

Fig. 1 presents a potential energy diagram for the various photolysis channels of both CH_3CHO and CF_3CHO . The minimum energy structures for the intact molecules are shown in the centre and various reaction pathways proceed to the left for CH_3CHO and to the right for CF_3CHO . The dashed horizontal line represents the energy of a 308 nm photon (388.4 kJ mol^{-1}), which is the wavelength employed in both the current and previous studies [8]. The potential energy schemes are strikingly similar. Several photodissociation channels are energetically open following 308 nm excitation, and there are no compelling differences that should preclude CF_3CHO from accessing the same rich ground state photochemistry as its non-fluorinated analogue.

Photolytic cleavage of the C–C bond via the well-known Norrish Type-I (NTI) reaction, produces CH_3/CF_3 and CHO (R1, green lines). This reaction is barrierless on the ground electronic state [18], requiring 347 and 335 kJ mol^{-1} for CH_3CHO and CF_3CHO , respectively. On the lowest energy triplet state, T_1 , the NTI reaction occurs over a small barrier (375 and 367 kJ mol^{-1} respectively). This pathway was not the focus of this study but we carefully studied the dynamics nonetheless since all previous work agrees that it is the dominant photolysis pathway for both species at 308 nm and it has not yet been explored for CF_3CHO . The details and results of these experiments are in the supplementary information Section S1 (including Figs. S2 & S3). The main conclusion is that the dynamics are the same for CH_3CHO and CF_3CHO and in accord with the predicted energetics in Fig. 1.

The decarbonylation pathways produce CO , accompanied by CH_4 or CHF_3 (R2, red lines) and are the focus of this study. These are the thermodynamically favoured products, lying 25 and 43 kJ mol^{-1} respectively below their precursors, but proceeding over high barriers of 347 and 325 kJ mol^{-1} , respectively. These pathways were investigated using resonance-enhanced multiphoton ionisation (REMPI) with velocity-mapped ion imaging (VMI) to probe CO photoproducts with quantum state specificity. We focus on the CO fragment because VMI depends on the target being ionised for detection, and CHF_3^+ is unstable and decomposes to CF_3^+ [19], which is already observed due to the radical channel (R1). These results are presented and discussed throughout the remaining sections of this article.

The most apparent difference in the photochemistry of these molecules is in the minor pathway producing $\text{CH}_2\text{CO} + \text{H}_2$ in CH_3CHO [20]. The transition state for the analogous pathway in CF_3CHO could not be located; instead a hydrogen-bonding interaction is formed between the formyl H-atom and a fluoromethyl

fluorine atom leading to CF_2 , HF and CO products. This predicted pathway has not been reported previously and has no analogue in the photochemistry of CH_3CHO , but is a (potential) competing source of CO photoproducts and needed to be investigated. We searched for this channel using carefully designed low-pressure Fourier-transform Infrared (FT-IR) experiments with *in situ* photolysis and found no evidence for it with a detection limit corresponding to a maximum possible quantum yield of $<0.07\%$. These experiments and analyses are described in detail in Section S2 (including Figs. S4, S5 & S6) of the supplementary information.

Dynamics of the decarbonylation channel (R2)

Fig. 2 summarises the key experimental results from this study. Fig. 2A shows the 2D REMPI spectrum of CO formed from photodissociation of CF_3CHO at 308 nm. The abscissa records the wavenumber of the CO detection laser on the lower axis and equivalent CO rotational quantum number, J , on the upper axis, and the ordinate shows the speed of the nascent CO . Two components are evident. The first appears in the lower left of Fig. 2A, outlined by the yellow triangle, and arises from slow CO with a narrow distribution of low- J states and is the dominant channel. The second component spans the entirety of Fig. 2A and reveals CO photoproducts with a broad distribution of speed and J . The 2D data in Fig. 2A can be integrated over either speed or wavelength as shown in Figs. 2B and 2C, respectively. Fig. 2B shows the 2D data integrated over low-speed (within the yellow triangle), high-speed and all-speed CO . Fig. 2C shows the orthogonal integration for low- J (within the yellow triangle), high- J and all- J . The data in both panels accentuate the bimodality in CO dynamics with low speed correlated with low J and high speed with high J .

This 2D REMPI spectrum is strikingly similar to that published previously for CH_3CHO [15]. The dissociation of CH_3CHO via R2 has been reported to occur via up to three different dynamical channels. Although the interpretation of each channel is still not agreed upon in the literature [15–17], the key factor for this work is that all hypothesised channels yield CH_4 and CO as photoproducts following dynamics on S_0 after initial photo-excitation to S_1 . The two different CO dynamical signatures from CF_3CHO dissociation in Fig. 2 are consistent with the multi-dynamical processes in CH_3CHO .

Quantum yield of the decarbonylation channel (R2)

From the experiments above, we conclude that R1 and R2 are active unimolecular photochemical decomposition pathways of CF_3CHO at 308 nm while there is no evidence for R3. We take advantage of the similar photochemistry of CF_3CHO and CH_3CHO , as demonstrated above, and the well-known photochemistry of the latter to determine the quantum yield (QY) of R2 under low pressure conditions. We utilise CH_3CHO as an internal standard with which we benchmark CF_3CHO . Three gas cylinders containing pure He, and either 2% CF_3CHO or CH_3CHO pre-mixed in He were prepared in a parallel gas manifold and placed immediately before the pulsed nozzle of the REMPI experiment described above. These gas mixtures could be switched in seconds while all other experimental parameters remained stable.

Fig. 3 shows the relative measurements of nascent CO ($J = 8$) signal from photolysis of each aldehyde as a function of time. Firstly, the CF_3CHO supply was switched on for 10 seconds and off for 10 seconds for 10 cycles. The feed gas was then switched to helium, showing the slightly lower background and verifying the removal of residual CF_3CHO . Finally, the feed gas was switched to CH_3CHO and a similar profile and reproducibility was observed. The relative intensity between CF_3CHO and CH_3CHO signal in Fig. 3, the absorption spectrum of each compound [21] and survey CO photoproduct REMPI spectra for each compound (Fig. S7 of the supplementary information) were then used to determine that the nascent (zero-pressure) quantum yield of R2 from CF_3CHO at 308 nm is 2.5 ± 0.7 times that of CH_3CHO . Further details about these calculations are in the supplementary information section S3.

Atmospheric fate of CF₃CHO

The results above demonstrate unambiguously that CHF₃ + CO is a primary product channel from the photolysis of CF₃CHO at 308 nm and that CF₃CHO and CH₃CHO exhibit analogous photochemistry. We utilise this to contextualise our results and to estimate the yield of CHF₃ under atmospheric conditions. Fig. 4 shows a summary of all previous measurements of the CH₃CHO and CF₃CHO quantum yields in air at atmospheric pressure. The most extensive data set for CH₃CHO was published by Moortgat and co-workers (MMW and WM) [13,14], while earlier measurements by Calvert and co-workers (HC and HKC) [11,12] are in good agreement. Panel A shows total photolysis QY, $\Phi(\text{tot})$, as a function of wavelength, while Panels B and C show $\Phi(\text{R1})$ and $\Phi(\text{R2})$ (*i.e.* the photolysis QYs for channels R1 and R2) separately.

The function fit through $\Phi(\text{tot})$ is the wavelength-pressure dependent quantum yield for CH₃CHO photodissociation recommended by IUPAC, calculated at atmospheric pressure [22]. There are no recommended functions for the individual quantum yields. IUPAC recommends $\Phi(\text{R2}) = 0$ for $\lambda > 300$ nm. However, the data in the inset to Fig. 4C show that, although the measured quantum yield at atmospheric pressure is small, it is not zero. The data shown here are consistent with the original publications [13,14], where the authors determine an upper limit of $\Phi(\text{R2}) < 0.005$. Although this small quantum yield has negligible implications for the atmospheric chemistry of CH₃CHO (which possibly led to the IUPAC recommendation), we argue below that this is not the case for CF₃CHO.

We fit a sigmoidal function to $\Phi(\text{R2})$ in Fig. 4C, while the line for $\Phi(\text{R1})$ in Fig. 4B is the difference between $\Phi(\text{tot})$ and $\Phi(\text{R2})$. We do not attribute any meaning to the functional form and the important aspect is the non-zero offset at $\lambda > 300$ nm, which is almost flat. Our sigmoidal fit places this at $\Phi(\text{R2}) = 0.004 \pm 0.002$.

Previous studies of the photochemistry of CF₃CHO are scarce. The available wavelength-dependent QYs for CF₃CHO are also shown in Fig. 4 [8,9]. We have demonstrated that the energetics and dynamics of these two carbonyl reactions are remarkably similar. Fig. 4 shows that this is translated through to equally similar QYs under atmospheric conditions. Fig. 4C includes an estimate of $\Phi(\text{R2})$ at 308 nm from this work. Here, we assume the collision-free measurement, $\Phi(\text{R2}, \text{CF}_3\text{CHO}) = 2.5 \times \Phi(\text{R2}, \text{CH}_3\text{CHO})$, also applies at atmospheric pressure, *i.e.* that the quenching kinetics for CH₃CHO and CF₃CHO are similar. This provides an estimate of $\Phi(\text{R2}) = 0.010 \pm 0.005$. The previous estimate of $\Phi(\text{R2}) = 0.021$ at 313 nm [9] lies a little above our estimate, as shown, but was recorded at lower pressure (700 Torr), with correspondingly less quenching and is therefore likely consistent with the present measurement.

The photolysis rate coefficient, k_{ph} , can be calculated as $k_{\text{ph}} = \sum_{\lambda} j(\lambda)\sigma(\lambda)\Phi(\lambda)$ where $j(\lambda)$ is the actinic flux, $\sigma(\lambda)$ the absorption cross section and $\Phi(\lambda)$ the photolysis quantum yield. Using the actinic flux for an overhead sun on a clear day from the US EPA [23], the published absorption spectrum of CF₃CHO [10] and the quantum yields from Fig. 4 evaluates to $k_{\text{ph}}(\text{tot}) = 5.9 \times 10^{-6} \text{ s}^{-1}$ and $k_{\text{ph}}(\text{R2}) = (7 \pm 4) \times 10^{-7} \text{ s}^{-1}$. CF₃CHO can also decompose in the atmosphere by reaction with OH with a reported rate coefficient, $k_{\text{OH}} = (4.8 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ [10]. Using the global average concentration of $[\text{OH}] = 1.1 \times 10^6 \text{ molecules cm}^{-3}$ [24] yields a pseudo-first order rate coefficient for reaction with OH of $k'_{\text{OH}} = 5.3 \times 10^{-7} \text{ s}^{-1}$. These rate coefficients govern the atmospheric fate of CF₃CHO resulting in a half-life of ~ 4 days with the dominant radical channel (R1) accounting for the removal of 79% of atmospheric CF₃CHO, 10% decomposing by reaction with OH and 11% of CF₃CHO in the atmosphere undergoing the decarbonylation reaction, R2, leading to CO and CHF₃ (HFC-23). Details of the calculations can be found in supplementary information Section S4, including Tables S1 & S2.

The photochemistry of CH₃CHO and CF₃CHO are fundamentally the same, however, the CH₄ pathway in CH₃CHO comprises only about 1% of the atmospheric fate, in comparison to the 11% calculated above for HFC-23 from CF₃CHO. The underlying difference is that the CH₃CHO reaction with OH has a rate coefficient ($k_{\text{OH}} = 1.5 \times 10^{-11} \text{ s}^{-1}$ [22]) that is over an order of magnitude greater than that for CF₃CHO. While CF₃CHO undergoes an average of 11 absorption cycles before reacting with OH and a 1% quantum yield becomes an 11% reaction fate, CH₃CHO absorbs only ~ 2 photons on average before reacting.

Implications for HFO use

We have determined that $\text{CHF}_3 + \text{CO}$ is unambiguously a primary photochemical product channel of CF_3CHO . Under collision-free conditions, the quantum yield is 2.5 times higher than for the equivalent channel in CH_3CHO . The dynamics, energetics and QYs of CF_3CHO are very similar to those of CH_3CHO . Utilising the more extensive data for CH_3CHO and the measurements in this work for CF_3CHO , we estimate the quantum yield of CHF_3 under atmospheric conditions to be $(1.0 \pm 0.5)\%$. Because the rate coefficient for reaction with OH is very slow, this 1% quantum yield results in $(11.0 \pm 5.5)\%$ of CF_3CHO molecules in the atmosphere decomposing via this CHF_3 pathway, resulting in a secondary $\text{GWP} = 1400 \pm 700$ for CF_3CHO .

CF_3CHO is formed in 100% molar yield from the atmospheric decomposition of HFO-1234ze [6] as well as from the decomposition of other HFOs [25] and HFCs [26]. This introduces a concern that HFOs being considered as replacement gases for air conditioning and other industrial uses might have significant impact as climate change agents. We note that if the GWP for CF_3CHO from this work withstands further scrutiny, the European Union would re-classify HFO-1234ze from a ‘low or no GWP’ compound into one that is forbidden [27].

At this stage, we refrain from recommending the withdrawal of HFO-1234ze from commercial use; there are too many uncertainties at present. The most significant uncertainty is using quantum yields from CH_3CHO as a proxy for CF_3CHO , despite the similarity shown in Fig. 4. More research is needed measuring the wavelength and pressure dependence of quantum yields for R1 and R2 for CF_3CHO explicitly and we call for urgent experiments in this regard.

In closing, we note that atmospheric monitoring has revealed an unknown source of HFC-23 over the past 3 years [3]. After decreasing for several years, the emission of CHF_3 in 2018 was higher than measured any year in history. The authors of that work explicitly suggest that China might not have met abatement targets. However, this study could provide an alternative explanation whereby legal production of HFOs might produce HFC-23 as a secondary atmospheric product thereby accounting for some of the observed increase.

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Figure 1: Potential energy scheme for the photodissociation of CF₃CHO and CH₃CHO. The CH₃CHO energies are experimental values from the references cited in the text and the CF₃CHO energies were calculated using the G4(MP2)-6x method [28]. The product and transition state energies are relative to the ground-state energy of the equilibrium geometry of each respective species. The dashed horizontal line represents the energy of a photon at 308 nm.

Figure 2: (A) 2D REMPI spectrum of the CO fragments formed following photolysis of CF₃CHO at 308 nm. B) CO REMPI spectra from integrating (A) at low speed (within the yellow triangle, red), high speed (outside the yellow triangle, blue) and all speeds (green). C) Speed distributions determined by integrating (A) within and without the yellow triangle and across all J .

Figure 3: Time-dependent CO ($J = 8$) ion signal as the molecular beam is switched on and off and from CF_3CHO to CH_3CHO as described in the text.

Figure 4: Comparison of quantum yields for CH_3CHO and CF_3CHO in 1 atm air, from various sources. [MMW: Reference [13]; WM: Reference [14]; HC: Reference [11]; HKC: Reference [12]. A) Total QY; B) QY for R1; C) QY for R2.

Methods

Experimental

In this work, we employed three experimental techniques to examine the three photochemical pathways, R1 to R3. Vacuum ultraviolet ionisation coupled with velocity-mapped ion imaging was used to investigate the CF_3 and CHO radical fragments from R1. Resonance-enhanced multiphoton ionization with VMI was used to probe CO photoproducts from R2. FT-IR spectroscopy was used to probe the HF products from R3.

The apparatus for all experiments has been described in detail previously [29,30,31] and the specific

details (including preparation of the target compound by a literature method [32]) are in Supplementary Information (Supplementary Methods section Figure S1). In brief, a molecular beam of 2% CF₃CHO or CH₃CHO in helium was passed into a VMI spectrometer. The early time component of this beam was intersected by a photolysis laser (308 nm), followed by an ionisation (detection) laser. Radical fragments (CF₃/CH₃ and CHO) from R1 were probed at 115 nm to ionise all quantum states of the radical of interest. CO from R2 was detected in specific quantum states at ~230 nm via REMPI. Nascent ions were separated in a time-of-flight mass spectrometer before impacting a position-sensitive MCP/phosphor screen detector, from which a kinetic energy distribution was determined. This is a collision free method that interrogates the unimolecular photochemistry of isolated molecules, providing true zero-pressure measurements. FT-IR experiments were conducted in a standard gas cell identifying end products following *in situ* photolysis at 308 nm.

Calculations

The geometry optimisations and energy calculations were carried out at the G4(MP2)-6x level of theory [28] using the Gaussian 09 (Revision D.01) software package [33]. Results were visualised using the open-source Avogadro molecular editor.

Methods References

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Author contributions

C.S.H. conceived the project. J.S.C. and C.S.H. designed and performed the experiments. All authors analysed and interpreted the results and contributed to the preparation of this manuscript.

Competing interest declaration

Authors declare no competing interests.

Additional information

Supplementary information is available for this paper at DOI:XXXX

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Figures

Figure 1

Potential energy scheme for the photodissociation of CF_3CHO and CH_3CHO . The CH_3CHO energies are experimental values from the references cited in the text and the CF_3CHO energies were calculated using the G4(MP2)-6x method [28]. The product and transition state energies are relative to the ground-state energy of the equilibrium geometry of each respective species. The dashed horizontal line represents the energy of a photon at 308 nm.

Figure 2

(A) 2D REMPI spectrum of the CO fragments formed following photolysis of CF_3CHO at 308 nm. B) CO REMPI spectra from integrating (A) at low speed (within the yellow triangle, red), high speed (outside the yellow triangle, blue) and all speeds (green). C) Speed distributions determined by integrating (A) within and without the yellow triangle and across all J .

Figure 3

Time-dependent CO ($J = 8$) ion signal as the molecular beam is switched on and off and from CF_3CHO to CH_3CHO as described in the text.

Figure 4

Comparison of quantum yields for CH_3CHO and CF_3CHO in 1 atm air, from various sources. [MMW: Reference [13]; WM: Reference [14]; HC: Reference [11]; HKC: Reference [12]. A) Total QY; B) QY for R1; C) QY for R2.

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