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Tropospheric photolysis of CF$_3$CHO

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HIGHLIGHTS

- Tropospheric photolysis of CF$_3$CHO investigated and photolysis products determined.
- Upper limit of 0.3% determined for the yield of CF$_3$H.
- Atmospheric fate of CF$_3$CHO discussed.

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ABSTRACT

Trifluoroacetaldehyde, CF$_3$CHO, is an atmospheric degradation product of several chlorofluorocarbon (CFC) alternatives. It is important to understand the further fate of CF$_3$CHO in the atmosphere. There is conflicting information on the CF$_3$CHO photolysis in the literature. In this chamber study, the tropospheric photolysis of CF$_3$CHO was investigated using broadband actinic radiation and FTIR spectroscopy for detection of the photolysis products. The photolysis produces CF$_3$ radicals in a yield of unity, which under atmospheric conditions gives dominantly COF$_2$ with smaller yields of oxides, alkoxy nitrates or per oxynitrates. No formation of CF$_3$H, HFC-23, was observed under any of the experimental conditions and an estimated upper limit for the yield of HFC-23 of 0.3% was established. Our results are in contradiction to those published most recently, which claimed to have observed HFC-23, and which has created a lot of debate in the scientific community. This is the first study of broadband UV photolysis of CF$_3$CHO, combined with FTIR detection of CF$_3$H.

1. Introduction

The photolysis of CF$_3$CHO has three principal pathways (Calvert et al., 2011):

\[
\begin{align*}
\text{CF}_3\text{CHO} + h\nu &\rightarrow \text{CF}_3 + \text{HCO} \quad (1a) \\
\text{CF}_3\text{CHO} + h\nu &\rightarrow \text{CF}_3\text{H} + \text{CO} \quad (1b) \\
\text{CF}_3\text{CHO} + h\nu &\rightarrow \text{CF}_3 + \text{CO} + \text{H} \quad (1c)
\end{align*}
\]

More than six decades ago, Dodd and Smith published the first results on the photolysis of CF$_3$CHO using 313-nm radiation (Dodd and Smith, 1957). They reported quantum yields of $\Phi_{1a} \sim 0.12$ and $\Phi_{1b} \sim 0.021$ at this wavelength. However, no evidence of reaction 1b was found by Pearce and Whytock (1971), also using 313-nm radiation. Richter et al.
observed CF$_2$H in the photolysis of CF$_3$CHO at 253.7 nm (Richter et al., 1992). Over the wavelength range 290–400 nm Sellevåg et al. (2004) reported the effective quantum yields of photolysis for CF$_3$CHO to be less than 0.02. Chiappero et al. (2006) reported a quantum yield of $\Phi_{1a} = (0.17 \pm 0.03)$ and no indication of reaction 1b occurring in the 308 nm photolysis of CF$_3$CHO. Recently Campbell et al. (2021) announced that they have observed a 308 nm quantum yield of $\Phi_{1b} = (0.010 \pm 0.005)$, meaning that actinic photolysis of CF$_3$CHO would be a source of CF$_2$H. CF$_2$H, has a global warming potential for the 100 year time horizon of GWP$_{100} = 12,960$ and could in effect present an additional secondary contribution to the radiative forcing of climate of the parent CFC alternatives. CF$_3$CHO is an intermediate degradation product in the atmospheric photo-oxidation of several CFC alternatives, e.g. CF$_3$CH$_2$CF$_2$H (HFC-365mfc) (Barry et al., 1995), ~100% yield, and E-CF$_3$CH=CHF (HFO-1234ze), 100% yield (Javadi et al., 2008). These alternatives, including the latest generation of Hydro Fluoro Olefins (HFOs) have been developed as key components in a strategy to lower the impact on climate from the 19.4 billion dollar (2021 US$) (Industrial Refrigeration, 2021) global industrial refrigeration system market. The refrigeration industry impacts many aspects of modern commerce. Hence, it is important to establish the yield of CF$_2$H in the tropospheric photolysis of CF$_3$CHO.

2. Experimental

The photoreactor used in this work consists of a 101-L quartz reactor connected to a Bruker IFS 66v/s FTIR spectrometer (Nilsson et al., 2009). Experiments were performed at 296 ± 5 K in 100 and 700 Torr of total pressure N$_2$, O$_2$ or air diluent. The IR spectra were derived from 32 co-added interferograms with a spectral resolution of 0.25 cm$^{-1}$ and an analytical path length of 40.35 m. The compounds were monitored using absorption features at several wavenumbers, e.g.: CH$_3$CHO: 1352, 1745 cm$^{-1}$, CF$_3$CHO: 706, 1787 cm$^{-1}$, CF$_2$H: 700, 1152 cm$^{-1}$, COF$_2$: 774, 1943 cm$^{-1}$ and CF$_3$NO: 1190, 1239 cm$^{-1}$. The photolysis was performed using Waldmann F85/100 UV6 lamps (wavelength region 290–400 nm). The spectral distribution of the output of these lamps is shown in Fig. 1 together with the solar actinic flux at the Earth surface (DeMore et al., 1997) and the absorption spectrum of CF$_3$CHO (Hashikawa et al., 2004). All reactant chemicals, except CF$_3$CHO, were obtained from commercial sources at purities > 99 %. CF$_3$CHO was synthesized by the dropwise addition of 10 g of the perfluoroaldehyde hydrate into a heated flask (T $\approx 60$ °C) containing 25 g of P$_2$O$_5$. Nitrogen gas was flowed slowly (approximately 20 cm$^3$ min$^{-1}$) over the heated hydrate/aldehyde mixture and through a liquid nitrogen trap, where CF$_3$CHO was collected and subsequently degassed via freeze–pump–thaw cycling. Quantification of CF$_3$NO, COF$_2$, CF$_2$O$_2$, CF$_3$, CF$_2$CF$_3$, CF$_2$ONO$_2$, CF$_2$O$_2$NO$_2$, and CF$_3$OH was achieved using published reference spectra from past studies, e.g., Nielsen et al. (1992) For the product yield plots and photolysis rate determination, quoted uncertainties include two standard deviations (2σ) of the linear least squares analysis together with a 3% uncertainty range associated with the analysis of the IR bands. Control experiments were performed in which reaction mixtures obtained after photolysis of CF$_3$CHO/NO/N$_2$/air and CF$_3$CHO/CH$_3$CHO/-NO/air/N$_2$ were left to stand in the dark in the chamber for 30 min. There was no observable loss ( < 1 %) of reactants and products, showing that heterogeneous reactions on the walls are not a significant complication in this work. Similarly, photolysis experiments were conducted using mixtures of CF$_3$H in air. No loss though photolysis of CF$_3$H was observed over a period of 1.5 h continued radiation with UV-B.

3. Results and discussion

3.1. UV-B photolysis of CF$_3$CHO in N$_2$ in the presence of NO

Of the three photolysis pathways, only reaction 1b yields CF$_2$H directly. In the absence of O$_2$, the produced CF$_3$ radicals from reactions 1a and 1c have two reaction pathways:
CF_3 + CF_3CHO → CF_3H + CF_3CO

Reaction 2 proceeds with a rate constant on the order of $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Vakhtin, 1996). There are no literature data for the rate coefficient for reaction (3). Experiments were performed using mixtures of 5.31–10.9 mTorr of CF$_3$CHO and 2.2–4.0 Torr of NO in 100–700 Torr of N$_2$ total pressure. Fig. 2 shows the formation of the products CF$_3$NO and COF$_2$ versus the loss of CF$_3$CHO following consecutive periods of UV-B photolysis. No CF$_3$F$_6$ was observed during these experiments. The large concentration of NO in these experiments ensures that CF$_3$ radicals produced in the dissociation will be scavenged effectively as CF$_3$NO ($k_4 \approx 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) (Vakhtin and Petrov, 1990):

CF$_3$ + NO + M → CF$_3$NO + M

As seen from Fig. 2, within the uncertainties, the initial molar yield of CF$_3$NO was indistinguishable from unity ($< 0.7$ mTorr consumption, 93 ± 10 % yield). Over the extended time duration for a single experiment (more than 2.5 h) photolysis CF$_3$NO may also occur in our chamber (Allston et al., 1978), in effect leading to a slow secondary loss of CF$_3$NO and reformation of CF$_3$ radicals. These will react again with NO or may react with small impurities of O$_2$ which lead to formation of COF$_2$ at the expense of CF$_3$NO through peroxy-alkoxy reaction sequences (see discussion below). The sum of CF$_3$NO and COF$_2$ observed during over the duration of these experiments gives a combined yield of (101 ± 4) %. CF$_3$H was not observed during the experiments, and an upper limit was determined as < 0.3 %. This suggests that reaction 1a is the dominant, if not sole, decomposition fate of the photolytically excited CF$_3$CHO.

3.2. Tropospheric photolysis of CF$_3$CHO in the presence of O$_2$ (with or without the presence of NO)

CO is a co-product of reaction 1a and 1c. In the presence of O$_2$, HCO formed in reaction 1a can also lead to the formation of CO. CO is easily detected in our chamber, and the formation CO was confirmed for all experiments. However, control experiments in which pure air was subjected to UV radiation resulted in observation of some amounts of CO and CO$_2$. This background formation is likely due to chamber surface reactions, and repeated flushing of the chamber reduced this effect, but could not eliminate it. This background formation of CO was unavoidable and variable. Since CO can be formed by all three reaction channels, it is not a good indirect marker for the formation of CF$_3$H (reaction 1b) in our system. For these reasons we do not account for the CO yield in these experiments.

The results of UV-B photolysis of 7.5–12 mTorr of CF$_3$CHO in 100 Torr of air, 700 Torr of oxygen or predominantly N$_2$ (< 1 Torr O$_2$ in 700 Torr of N$_2$) are shown in Fig. 3A. As seen from Fig. 3A, consistent results were obtained in the presence of 1–700 Torr of O$_2$ or N$_2$. There was no discernible difference in the product distribution between experiments conducted in air at 100 Torr and at 700 total pressures, which suggests that O$_2$ is an effective scavenger of CF$_3$ radicals generated in the system. In the absence of NOx, the produced CF$_3$ radical will react with O$_2$ through a well-known mechanism that involves several different pathways:

CF$_3$ + O$_2$ + M → CF$_3$O$_2$ + M

CF$_3$O$_2$ + CF$_3$O$_2$ + M → 2CF$_3$O + O$_2$ + M

CF$_3$O$_2$ + CF$_3$O + M → CF$_3$O$_3$CF$_3$ + M

Fig. 2. The formation of products, CF$_3$NO (triangles) and COF$_2$ (squares) versus loss of CF$_3$CHO during UV-B photolysis of CF$_3$CHO–NO–N$_2$ mixtures at 296 ± 5 K. Dashed lines are polynomial fits to the datapoints for CF$_3$NO and COF$_2$ to aid the eye. Open circles represent the sum of the data for CF$_3$CN and COF$_2$. The solid line is a linear least squares fit to the summed data. The datapoint shown for the formation of CF$_3$H (diamond) illustrates the estimated upper limit for the formation of this species.
CF₃O + CF₃O + M → CF₃O₂CF₃ + M \hspace{1cm} (8)

CF₃O + RH → CF₃OH + R \hspace{1cm} (9)

CF₃OH → COF₂ + HF \hspace{1cm} (10)

In the scheme above, RH represents any hydrogen containing species in the chamber. Linear least squares analysis of the data for the sum of COF₂ and oxides/hydroxide (CF₃O₂CF₃, CF₃O₂CF₂ and CF₃OH) gave a combined yield of (102 ± 4) %. This suggests that reaction 1a (and possibly 1c) accounts for all the quantum yield of the reaction. No formation of CF₃H was observed in these experiments and we estimate an upper limit of 0.3 % for the formation of CF₃H.

There is a possibility that CF₃O radicals, generated in reaction 6, could react with CF₃CHO as in reaction 9, leading to unwanted loss of CF₃CHO. We performed a series of experiments with mixtures of 6.94–7.96 mTorr of CF₃CHO and 3.4–4.5 mTorr of NO added to prevent such unwanted reactions:

CF₃O₂ + NO → CF₃O + NO₂ \hspace{1cm} (11)

CF₃O + NO → COF₂ + FNO \hspace{1cm} (12)

In these experiments small quantities of peroxy- and alkoxy-nitrates were formed due to the following reaction pathways:

CF₃O₂ + NO₂ + M → CF₃O₂NO₂ + M \hspace{1cm} (13)

CF₃O + NO₂ + M → CF₃ONO₂ + M \hspace{1cm} (14)

Fig. 3. Product yields during the UV-B photolysis of 7.5–12 mTorr of CF₃CHO in Panel A: in 700 Torr of O₂ (solid symbols), 100 Torr of air (gray symbols) or in 1 Torr of O₂ in mixture with N₂ (700 Torr total pressure, open symbols), and Panel B: in 100 Torr (gray symbols) or 700 Torr (cross-haired gray symbols) of air with added NO. Dashed/dotted lines are polynomial fits to the data to aid the eye, whereas solid lines are linear least squares fits to the data. All experiments were performed at 296 ± 5 K.
Various amounts of alkyl- and peroxy-nitrates were observed. The formation of these nitrate compounds and COF accounts for the reaction channels 1a and 1c and sums to (96 ± 4)%. As seen from Fig. 3B, the results obtained in the presence of NO are consistent with those obtained in the absence of NOx (Panel A of Fig. 3), including the absence of any positive identification of CF₃H. We estimate an upper limit of 0.3% for the CF₃H yield in the presence of NO.

3.3. Overall quantum yield for CF₃CHO

A determination of the overall photolysis quantum yield for process 1 was performed using CH₃CHO as a chemical actinometer. CH₃CHO has been employed previously in our chamber as a reference compound to measure relative photolysis rates (Sulbaek Andersen et al., 2018). Reaction mixtures consisting of 6.87–24.91 mTorr of CF₃CHO and CH₃CHO and 0–10.16 mTorr of NO in 100 or 700 Torr total pressure of air were irradiated for up to 90 min using UV-B radiation. The reactant consumption followed first-order decay for the two compounds. Fig. 4 shows the decay of CF₃CHO versus the decay of CH₃CHO following repeated UV-B radiation exposures. As seen from here there was no observable difference between the data obtained over the range of 100–700 Torr total pressure, nor in the presence or absence of NO. Linear least squares fit to the data shown in Fig. 4 gives a relative photolysis rate of (0.443 ± 0.013), i.e., the photolysis of CF₃CHO over the wavelength range 290–400 nm, occurs at a rate which is roughly half that of CH₃CHO.

Quantum yields are wavelength dependent, and as the radiation source used in the present work is broadband in nature (290–400 nm, see Fig. 1), the relative photolysis rate measured above reflect an integrated quantum yield for the irradiation wavelength range, see equation (1):

$$\frac{J_{\text{CF}_3\text{CHO}}}{J_{\text{CH}_3\text{CHO}}} = \frac{\Phi_{\text{CF}_3\text{CHO}}(290-400 \text{ nm}) \times \sigma_{\text{CF}_3\text{CHO}, 290-400 \text{ nm}}}{\Phi_{\text{CH}_3\text{CHO}}(290-400 \text{ nm}) \times \sigma_{\text{CH}_3\text{CHO}, 290-400 \text{ nm}}}$$  \hspace{1cm} (1)

In the absence of relative photolysis rates measured at discrete wavelengths, an approximation can be made in which the relative photolysis rate is assumed to be independent of wavelength over the range of irradiation. Then an estimated quantum yield can be calculated at discrete wavelengths using a scaling that involves the UV cross-sections for CF₃CHO and CH₃CHO (DeMore et al., 1997) and the wavelength dependent quantum yields for the analogous reactions, 1a though 1c, for CH₃CHO, as shown in Fig. 5. Using this approach, the total quantum yield for CF₃CHO at 308 nm is estimated to be 0.16, based on σ(CF₃CHO, 308 nm) = $2.97 \times 10^{20}$ cm$^2$ molecule$^{-1}$. The majority of photofragments observed are due to dissociation processes occurring as a result of absorption of photons towards the lower end of our radiation source (290–320 nm range). The quantum yield of 0.02 for reaction 1a, at 308 nm, measured by Sellevåg et al. (2004) appears to be in error. The results obtained in this work, under three different conditions, in 100–700 Torr of NO/N$_2$, in mixtures with 1–700 Torr O$_2$ and in the presence NOx, all give a consistent picture of the photolysis product yields during the UV-B photolysis of CF₃CHO. No evidence was obtained to indicate the occurrence of reaction 1b under tropospheric photolysis conditions. This is contrary to the findings of $\Phi_{1b} = 0.010$ stated by Campbell et al. (2021) The product distributions are consistent with the majority of the photofragmentation occurring via channel 1a with the possibility of some contribution from reaction 1c.

4. Conclusion

Our results show no detectable (< 0.3%) CF₃H produced during the tropospheric photolysis of CF₃CHO. This suggests that pathway 1b is of no significant importance for the photolysis of CF₃CHO from 400 nm down to 290–300 nm. This has important implications for the understanding of the atmospheric photo-oxidation mechanisms of several CFC alternatives. The current interest centers around the disagreements between the results published in the literature (Dodd and Smith, 1957;
Pearce and Whytock, 1971; Richter et al., 1992; Sellevåg et al., 2004; Chiappero et al., 2006; Campbell et al., 2021. It is important to realize that the five previous studies and the present investigation were performed using different photolysis sources and detection methods. Hence, a direct comparison of the results is difficult. Diluents (air, N₂, and O₂), pressures (100–700 Torr), and broadband UV (wavelengths of 290–400 nm) used in the present work are experimental conditions directly relevant for the tropospheric photolysis of CF₃CHO, i.e. for photochemical processes occurring in the atmosphere from surface to below the tropopause (0–15 km altitude). Photolysis of CF₃CHO at lower wavelengths relevant to the upper troposphere/lower stratosphere should be further investigated before it can be included in future high altitude atmospheric modelling.

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Mads Peter Sulbaek Andersen: Conceptualization, data acquisition, Formal analysis, Project administration, Writing – original draft, Writing – review & editing. Ole John Nielsen: Conceptualization, data acquisition, Formal analysis, Project administration, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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