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Tropospheric photolysis of CF$_3$CHO

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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 peroxynitrates. 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):

CF$_3$CHO + h$\nu$ $\rightarrow$ CF$_3$ + HCO

(1a)

CF$_3$CHO + h$\nu$ $\rightarrow$ CF$_3$H + CO

(1b)

CF$_3$CHO + h$\nu$ $\rightarrow$ CF$_3$ + CO + H

(1c)

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$_3$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$_3$H. CF$_3$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 from 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 refrigeration industry impacts many aspects of modern commerce. Hence, it is important to establish the yield of CF$_3$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$_3$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$_3$O$_2$CF$_3$, CF$_3$O$_2$CF$_3$, CF$_3$ONO$_2$, CF$_3$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$_3$H directly. In the absence of O$_2$, the produced CF$_3$ radicals from reactions 1a and 1c have two reaction pathways:

![Fig. 1. Spectral overlay of the sun actinic flux in the lower troposphere (dotted line) (DeMore et al., 1997), the photolysis radiation source used in the present experiments (solid line) and the UV- absorption cross section for CF$_3$CHO (dashed line) (Hashikawa et al., 2004).](image-url)
CF$_3$ + CF$_3$CHO → CF$_3$H + CF$_3$CO

Reaction 2 proceeds with a rate constant on the order of $10^{-12}$ cm$^3$/molecule·s$^{-1}$. 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$_3$NO 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·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 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$_2$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.
\[ \text{CF}_3\text{O} + \text{CF}_3\text{O} + \text{M} \rightarrow \text{CF}_3\text{O}_2\text{CF}_3 + \text{M} \]  
(8)

\[ \text{CF}_3\text{O} + \text{RH} \rightarrow \text{CF}_3\text{OH} + \text{R} \]  
(9)

\[ \text{CF}_3\text{OH} \rightarrow \text{COF}_2 + \text{HF} \]  
(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 (CF3OOCF3, CF3OOOCF3 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:

\[ \text{CF}_3\text{O}_2 + \text{NO} \rightarrow \text{CF}_3\text{O} + \text{NO}_2 \]  
(11)

\[ \text{CF}_3\text{O} + \text{NO} \rightarrow \text{COF}_2 + \text{FNO} \]  
(12)

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

\[ \text{CF}_3\text{O}_2 + \text{NO}_2 + \text{M} \rightarrow \text{CF}_3\text{O}_2\text{NO}_2 + \text{M} \]  
(13)

\[ \text{CF}_3\text{O} + \text{NO}_2 + \text{M} \rightarrow \text{CF}_3\text{ONO}_2 + \text{M} \]  
(14)
Various amounts of alkyl- and peroxy-nitrates were observed. The formation of these nitrates compounds and COF$_2$ 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 CF$_3$H. We estimate an upper limit of 0.3 % for the CF$_3$H yield in the presence of NO.

3.3. Overall quantum yield for CF$_3$CHO

A determination of the overall photolysis quantum yield for process 1 was performed using CH$_2$CHO as a chemical actinometer. CH$_2$CHO 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 CF$_3$CHO and CH$_2$CHO 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 (I) source used in the present work is broadband in nature (290–400 nm), the relative photolysis rate measured above reflect an integrated quantum yield for the irradiation wavelength range, see equation (1):

$$\frac{J_{\text{CF}_3\text{CHO}}}{J_{\text{CH}_2\text{CHO}} \text{measured}} = \frac{\phi_{\text{CF}_3\text{CHO}} 290–400 \text{ nm}}{\phi_{\text{CH}_2\text{CHO}} 290–400 \text{ nm}} \times \frac{\sigma_{\text{CF}_3\text{CHO}} 290–400 \text{ nm}}{\sigma_{\text{CH}_2\text{CHO}} 290–400 \text{ nm}}$$

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 CF$_2$CHO and CH$_2$CHO (DeMore et al., 1997) and the wavelength dependent quantum yields for the analogous reactions, 1a though 1c, for CH$_2$CHO, as shown in Fig. 5 (Calvert et al., 2008). Using this approach, the total quantum yield for CF$_3$CHO at 308 nm is estimated to be 0.16, based on $\sigma$(CF$_3$CHO, 308 nm) = 2.97 × 10$^{20}$ cm$^2$ molecule$^{-1}$, $\phi$(CF$_3$CHO, 308 nm) = 0.325, and $\sigma$(CH$_2$CHO, 308 nm) = 3.31 × 10$^{20}$ cm$^2$ molecule$^{-1}$. This value is nearly identical to that measured by Chiappero et al. (2006) who used a 308-nm pulsed laser radiation source and reported 0.17 for the 308 nm quantum yield. This suggests that a) the overall quantum yield for CF$_3$CHO has a wavelength dependency similar to that of CH$_2$CHO and b) 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 CF$_3$CHO. 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%) CF$_3$H produced during the tropospheric photolysis of CF$_3$CHO. This suggests that pathway 1b is of no significant importance for the photolysis of CF$_3$CHO 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, N\textsubscript{2} and O\textsubscript{2}), 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 CF\textsubscript{3}CHO, i.e. for photochemical processes occurring in the atmosphere from surface to below the tropopause (0–15 km altitude). Photolysis of CF\textsubscript{3}CHO at lower wavelengths relevant to the upper troposphere/lower stratosphere should be further investigated before it can be included in future high altitude atmospheric modeling.

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**CRediT authorship contribution statement**

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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