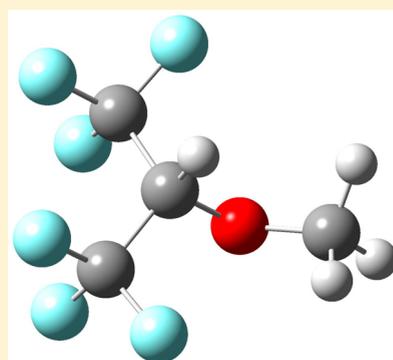


Atmospheric Chemistry of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ Freja From Østerstrøm,<sup>†</sup> Timothy J. Wallington,<sup>\*,‡</sup> Mads P. Sulbaek Andersen,<sup>†,§</sup> and Ole John Nielsen<sup>†</sup><sup>†</sup>Copenhagen Center for Atmospheric Research, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark<sup>‡</sup>Research and Advanced Engineering, Ford Motor Company, Dearborn, Michigan 48121-2053, United States<sup>§</sup>Department of Chemistry and Biochemistry, California State University, Northridge, California 91330, United States

## Supporting Information

**ABSTRACT:** Smog chambers with in situ FTIR detection were used to measure rate coefficients in 700 Torr of air and  $296 \pm 2$  K of:  $k(\text{Cl}+(\text{CF}_3)_2\text{CHOCH}_3) = (5.41 \pm 1.63) \times 10^{-12}$ ,  $k(\text{Cl}+(\text{CF}_3)_2\text{CHOCHO}) = (9.44 \pm 1.81) \times 10^{-15}$ ,  $k(\text{Cl}+\text{CF}_3\text{C}(\text{O})\text{OCH}_3) = (6.28 \pm 0.98) \times 10^{-14}$ ,  $k(\text{OH}+(\text{CF}_3)_2\text{CHOCH}_3) = (1.86 \pm 0.41) \times 10^{-13}$ , and  $k(\text{OH}+(\text{CF}_3)_2\text{CHOCHO}) = (2.08 \pm 0.63) \times 10^{-14}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The Cl atom initiated oxidation of  $(\text{CF}_3)_2\text{CHOCH}_3$  gives  $(\text{CF}_3)_2\text{CHOCHO}$  in a yield indistinguishable from 100%. The OH radical initiated oxidation of  $(\text{CF}_3)_2\text{CHOCH}_3$  gives the following products (molar yields):  $(\text{CF}_3)_2\text{CHOCHO}$  ( $76 \pm 8$ %),  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  ( $16 \pm 2$ %),  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  ( $4 \pm 1$ %), and  $\text{C}(\text{O})\text{F}_2$  ( $45 \pm 5$ %). The primary oxidation product  $(\text{CF}_3)_2\text{CHOCHO}$  reacts with Cl atoms to give secondary products (molar yields):  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  ( $67 \pm 7$ %),  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  ( $28 \pm 3$ %), and  $\text{C}(\text{O})\text{F}_2$  ( $118 \pm 12$ %).  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  reacts with Cl atoms to give:  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  ( $80 \pm 8$ %) and  $\text{C}(\text{O})\text{F}_2$  ( $6 \pm 1$ %). Atmospheric lifetimes of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  were estimated to be 62 days, 1.5 years, and 220 days, respectively. The 100-year global warming potentials (GWPs) for  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  are estimated to be 6, 121, and 46, respectively. A comprehensive description of the atmospheric fate of  $(\text{CF}_3)_2\text{CHOCH}_3$  is presented.



## 1. INTRODUCTION

Chlorofluorocarbons (CFCs) were developed and found use in various applications including refrigeration, conditioning, foam blowing, and electronics cleaning.<sup>1</sup> CFCs are unreactive in the troposphere but undergo photolysis in the stratosphere leading to chlorine-based catalytic ozone destruction.<sup>2,3</sup> Springtime depletion of stratospheric ozone over Antarctica known as the “Ozone Hole” reflects the adverse environmental impact of CFCs.<sup>4</sup> The use of CFCs has been phased out under the Montreal Protocol, and a variety of replacement compounds have been introduced. Hydrofluoroethers (HFEs) are one class of CFC replacements. HFEs do not contain chlorine and hence do not contribute to chlorine-based catalytic ozone destruction. HFEs generally have shorter atmospheric lifetimes and hence smaller global warming potentials than the CFCs they replace. Prior to the large scale use of HFEs it is desirable to establish a complete understanding of their atmospheric chemistry and environmental impact.

We report the results of a comprehensive study of the atmospheric chemistry of  $(\text{CF}_3)_2\text{CHOCH}_3$  (1,1,1,3,3,3-hexafluoro-2-methoxypropane). The kinetics and products of the gas-phase reactions of Cl atoms and OH radicals with  $(\text{CF}_3)_2\text{CHOCH}_3$  and  $(\text{CF}_3)_2\text{CHOCHO}$  (2,2,2-trifluoro-1-(trifluoromethyl)ethyl formate) were determined at the Copenhagen Center for Atmospheric Research at University of Copenhagen (CCAR). The kinetics and products of

reactions of Cl atoms with  $(\text{CF}_3)_2\text{CHOCH}_3$  were studied at Ford Motor Company (Ford). The kinetics and products of reactions of Cl atoms with  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  (methyl trifluoroacetate) were studied at CCAR.

The kinetics of the reaction of OH radicals with  $(\text{CF}_3)_2\text{CHOCH}_3$  have been studied previously by Oyaró et al.<sup>5</sup> and Chen et al.,<sup>6</sup> however, there is a factor of approximately 2 difference in the results reported in these previous studies. One of the goals of the present work was to resolve this discrepancy. A large family of fluorinated ethers have been studied in the past, including  $\text{CF}_3\text{OCH}_3$ ,  $\text{CF}_3\text{CH}_2\text{OCH}_3$ ,  $\text{C}_2\text{F}_5\text{CH}_2\text{OCH}_3$ ,  $\text{CF}_3\text{CF}_2\text{OCH}_3$ ,  $(\text{CF}_3)_2\text{CFOCH}_3$ ,  $n\text{-C}_3\text{F}_7\text{OCH}_3$ ,  $n\text{-C}_4\text{F}_9\text{OCH}_3$ ,  $i\text{-C}_4\text{F}_9\text{OC}_2\text{H}_5$ , and  $n\text{-C}_4\text{F}_9\text{OC}_2\text{H}_5$ .<sup>7–14</sup> The data presented here for  $(\text{CF}_3)_2\text{CHOCH}_3$  further extend our knowledge of the atmospheric chemistry of HFEs and facilitate discussions of the impact of molecular structure on atmospheric chemistry of HFEs.

## 2. EXPERIMENTAL METHOD

The Ford smog chamber is a 140 L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer.<sup>15</sup> The smog chamber is surrounded by 22 fluorescent blacklight GE F40BLB lamps

Received: August 23, 2015

Revised: October 1, 2015

used to initiate the reactions. The analytical path length of the Ford smog chamber is 27.6 m. The CCAR photoreactor is a 101 L quartz reactor interfaced with a Bruker IFS 66v/s FTIR spectrometer.<sup>16</sup> 8 UVA and 16 UVC lamps surrounding the CCAR chamber were used to photochemically initiate the experiments. The CCAR analytical path lengths used in this study were 50.34 to 53.42 m.

For both experimental setups the spectral resolution of the FTIR spectrometers was 0.25 cm<sup>-1</sup>, and all experiments were performed at a total pressure of 700 Torr of air/N<sub>2</sub>/O<sub>2</sub> diluent at 296 ± 2 K. Infrared spectra were derived from 32 coadded interferograms. Reactant and reference compounds were monitored using absorption features over the wavenumber ranges listed in the [Supporting Information](#).

In both systems, Cl atoms were produced from the photolysis of Cl<sub>2</sub>:

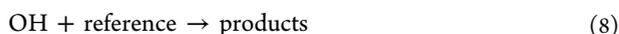


In the CCAR reaction chamber OH radicals were produced by photolysis of O<sub>3</sub> in the presence of H<sub>2</sub>:



Ozone was produced using a commercial ozone generator from O<sub>3</sub>-Technology. The ozone was preconcentrated using a silica gel trap, reducing the amount of O<sub>2</sub> introduced into the chamber.

In relative rate experiments the following reactions take place:



It can be shown that

$$\ln\left(\frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t}\right) = \frac{k_{\text{reactant}}}{k_{\text{reference}}}\ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right) \quad (1)$$

where [reactant]<sub>t<sub>0</sub></sub>, [reactant]<sub>t</sub>, [reference]<sub>t<sub>0</sub></sub>, and [reference]<sub>t</sub> are the concentrations of the reactant and the reference at times t<sub>0</sub> and t, and k<sub>reactant</sub> and k<sub>reference</sub> are the rate coefficients for the reactant and the reference. Plots of ln([reactant]<sub>t<sub>0</sub></sub>/[reactant]<sub>t</sub>) versus ln([reference]<sub>t<sub>0</sub></sub>/[reference]<sub>t</sub>) should be linear, pass through the origin, and have a slope of k<sub>reactant</sub>/k<sub>reference</sub>.

(CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub> and CF<sub>3</sub>C(O)OCH<sub>3</sub> were supplied by 3M at a purity of ≥99% and subjected to several freeze–pump–thaw cycles before use. (CF<sub>3</sub>)<sub>2</sub>CHOCHO was produced in the photoreactor at CCAR. Ultrapure N<sub>2</sub>, O<sub>2</sub>, and synthetic air was used as received. All other reagents were obtained from commercial sources. No impurities were observed using the FTIR spectrometer.

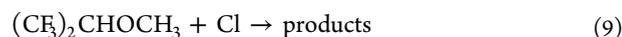
In smog chamber experiments it is important to check for unwanted loss of reactants and products via photolysis, dark chemistry, and heterogeneous reactions. Control experiments were performed at Ford and CCAR in which mixtures of reactants (except Cl<sub>2</sub>) in air were subjected to UV irradiation

for 15 min and reactant/product mixtures obtained after the UV irradiation were allowed to stand in the dark in the chamber for 30 min. There was no observable loss of reactants or reference compounds, suggesting that photolysis, dark chemistry, and heterogeneous reactions are not a significant complication in the present work.

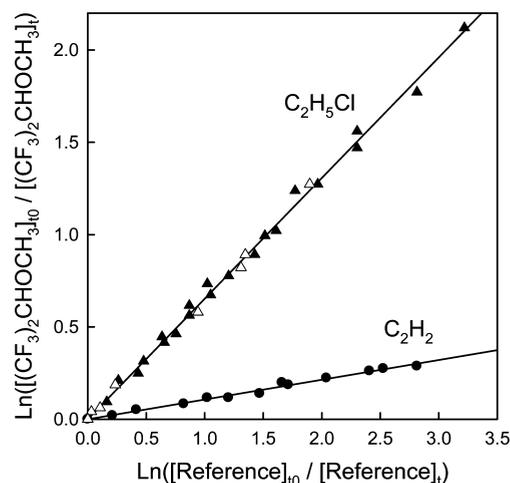
Unless otherwise stated, quoted uncertainties are two standard deviations from the least-squares regressions (forced through zero), together with our estimated uncertainties (±1% of the initial concentration) associated with the IR spectral analysis of the relative reactant and reference concentrations.

### 3. RESULTS AND DISCUSSION

**3.1. Relative Rate Study of (CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub> + Cl.** The reaction of (CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub> with Cl atoms was studied using relative rate methods at Ford and CCAR. At Ford initial reaction mixtures consisted of 10.6–17.3 mTorr of (CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub>, 148.4–151 mTorr of Cl<sub>2</sub>, either 33.4–35.6 mTorr of C<sub>2</sub>H<sub>5</sub>Cl or 9.40 mTorr of C<sub>2</sub>H<sub>2</sub>, and 0–140 Torr of O<sub>2</sub> in a total pressure of 700 Torr made up using N<sub>2</sub> diluent. At CCAR reactant mixtures consisted of 3.23–11.5 mTorr of (CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub>, 52.7–157.4 mTorr of Cl<sub>2</sub> and 6.67–34.4 mTorr of C<sub>2</sub>H<sub>5</sub>Cl with 140 Torr of O<sub>2</sub> in a total pressure of 700 Torr of air. The rate of reaction 9 was measured relative to reactions 10 and 11:



The observed loss of (CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub> versus that of the reference compounds in the presence of Cl atoms is shown in [Figure 1](#). The values obtained using different experimental



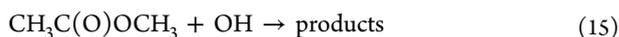
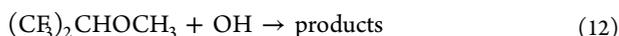
**Figure 1.** Decay of (CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub> versus the reference compounds C<sub>2</sub>H<sub>5</sub>Cl (triangles) and C<sub>2</sub>H<sub>2</sub> (circles) in the presence of Cl atoms in 700 Torr of air. Filled symbols are data from Ford; open symbols are data from CCAR.

setups at Ford (solid symbols) and CCAR (open symbols) were, within the experimental uncertainties, indistinguishable. Linear least-squares analysis of the data in [Figure 1](#) gives rate coefficient ratios of k<sub>9</sub>/k<sub>10</sub> = (0.65 ± 0.07) and k<sub>9</sub>/k<sub>11</sub> = (0.11 ± 0.01). Using the reference rate coefficients k<sub>10</sub>(Cl+C<sub>2</sub>H<sub>5</sub>Cl) = (8.27 ± 2.11) × 10<sup>-12</sup><sup>17</sup> and k<sub>11</sub>(Cl+C<sub>2</sub>H<sub>2</sub>) = (5.07 ± 0.34) ×

$10^{-11}$ <sup>18</sup> gives  $k_9(\text{Cl}+(\text{CF}_3)_2\text{CHOCH}_3) = (5.41 \pm 1.48) \times 10^{-12}$  and  $(5.42 \pm 0.67) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We choose to report a final rate coefficient as the average of the two determinations with an uncertainty that encompasses the extremes of the individual determinations. Hence,  $k_9(\text{Cl}+(\text{CF}_3)_2\text{CHOCH}_3) = (5.41 \pm 1.63) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Oyaro et al. have reported a rate coefficient of  $k_9(\text{Cl}+(\text{CF}_3)_2\text{CHOCH}_3) = (8.4 \pm 1.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>5</sup> This value is 55% larger than that determined in the present study. Oyaro et al. used a relative rate technique with  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CH}_2\text{OH}$  as reference compounds. As discussed by Thomsen et al.,<sup>9</sup> there is an internal inconsistency in the results reported by Oyaro et al.<sup>5</sup> with the more fluorinated compound  $\text{CF}_3\text{CF}_2\text{CH}_2\text{OCH}_3$  reported to be substantially more reactive than the less fluorinated compound  $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCH}_3$ . Such a trend of increasing reactivity with increasing fluorination in these molecules runs counter to chemical intuition and, together with the discrepancy in the value of  $k_9$  noted above, suggests that there may have been systematic errors in the work of Oyaro et al.<sup>5</sup>

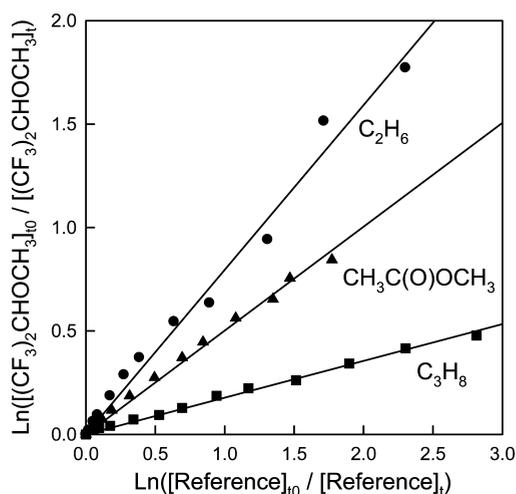
It is interesting to compare the reactivity of Cl atoms toward  $(\text{CF}_3)_2\text{CHOCH}_3$  and  $(\text{CF}_3)_2\text{CFOCH}_3$ .<sup>10</sup> The rate coefficient for the reaction of Cl atoms with  $(\text{CF}_3)_2\text{CFOCH}_3$  has been determined by Andersen et al.:<sup>10</sup>  $k(\text{Cl}+(\text{CF}_3)_2\text{CFOCH}_3) = (1.80 \pm 0.42) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Substitution of the middle hydrogen atom in  $(\text{CF}_3)_2\text{CHOCH}_3$  by a fluorine atom to give  $(\text{CF}_3)_2\text{CFOCH}_3$  results in a 30-fold reduction in the reactivity of the molecule toward Cl atoms.

**3.2. Relative Rate Study of  $(\text{CF}_3)_2\text{CHOCH}_3 + \text{OH}$ .** Using the CCAR smog chamber, the rate of reaction 12 was measured relative to those of (reactions 13–15). Initial reactant concentrations were 3.0–3.1 mTorr of  $(\text{CF}_3)_2\text{CHOCH}_3$ , 2.0–4.4 Torr of  $\text{O}_3$ , 287–570 mTorr of  $\text{H}_2$ , and either 14.3 mTorr of  $\text{C}_2\text{H}_6$ , 11.5 mTorr of  $\text{C}_3\text{H}_8$ , or 5.5 mTorr of  $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ , in 700 Torr of air.



Linear regressions of the data in Figure 2 give  $k_{12}/k_{13} = (0.796 \pm 0.090)$ ,  $k_{12}/k_{14} = (0.178 \pm 0.018)$ , and  $k_{12}/k_{15} = (0.502 \pm 0.053)$ . The rate coefficient ratios determined above can be put on an absolute scale using the OH radical rate coefficients for the three reference compounds. Using  $k_{13}(\text{OH}+\text{C}_2\text{H}_6) = (2.41 \pm 0.08) \times 10^{-13}$ ,<sup>19</sup>  $k_{14}(\text{OH}+\text{C}_3\text{H}_8) = (1.09 \pm 0.08) \times 10^{-12}$ ,<sup>19</sup> and  $k_{15}(\text{OH}+\text{CH}_3\text{C}(\text{O})\text{OCH}_3) = (3.41 \pm 0.29) \times 10^{-13}$ ,<sup>20</sup> gives  $k_{12}(\text{OH}+(\text{CF}_3)_2\text{CHOCH}_3) = (1.92 \pm 0.23) \times 10^{-13}$ ,  $(1.94 \pm 0.25) \times 10^{-13}$ , and  $(1.71 \pm 0.23) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. Results obtained using the three different reference compounds were indistinguishable within the experimental uncertainties, suggesting the absence of significant systematic errors in the present work. We choose to report a final value for  $k_{12}$  as the average of the three determinations with error limits which encompass the extremes of the individual determinations. Hence,  $k_{12}(\text{OH}+(\text{CF}_3)_2\text{CHOCH}_3) = (1.86 \pm 0.41) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Chen et al.<sup>6</sup> and Oyaro et al.<sup>5</sup> have reported values of  $k_{12}$  of  $(2.25 \pm 0.04) \times 10^{-13}$  and  $(1.27 \pm 0.13) \times 10^{-13} \text{ cm}^3$



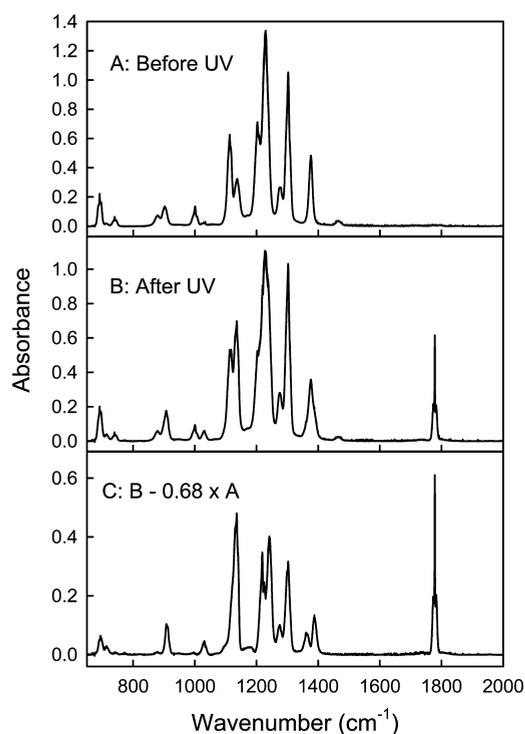
**Figure 2.** Decay of  $(\text{CF}_3)_2\text{CHOCH}_3$  versus  $\text{C}_2\text{H}_6$  (circles),  $\text{C}_3\text{H}_8$  (squares), and  $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$  (triangles) in the presence of OH radicals in 700 Torr of air.

$\text{molecule}^{-1} \text{ s}^{-1}$ , respectively. Our result is consistent with the value reported by Chen et al.,<sup>6</sup> but is significantly higher (46%) than that reported by Oyaro et al.<sup>5</sup> We use three different compounds with well-known rate coefficients for a robust determination of  $k_{12}$ . Oyaro et al. used  $\text{CH}_2\text{Cl}_2$  and the commercial mixture of *n*- and *i*- $\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$  (HFE-7200) as reference compounds.  $\text{CH}_2\text{Cl}_2$  as a reference for OH reaction kinetics is a poor choice as it is well established that the oxidation of  $\text{CH}_2\text{Cl}_2$  releases chlorine atoms. Given the high reactivity of chlorine atoms toward  $(\text{CF}_3)_2\text{CHOCH}_3$ , the presence of chlorine atoms would lead to an overestimate of the OH reactivity by Oyaro et al., and so this does not explain the discrepancy between our results and those of Oyaro et al. The kinetics of the reaction of OH with HFE-7200 has been the subject of two studies with results differing by approximately a factor of 2. Oyaro et al.<sup>5</sup> used the rate coefficient reported by Oyaro and Nielsen.<sup>21</sup> If Oyaro et al.<sup>5</sup> had instead used the rate coefficient reported by Christensen et al.,<sup>13</sup> their result for  $k_{12}$  would be approximately  $9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Again we are not able to explain the discrepancy between our results and those from Oyaro et al. Given the consistency of our results with those from Chen et al.,<sup>6</sup> and the complications in interpreting the data from Oyaro et al. noted above, we conclude that there were systematic errors in the determination of  $k_{12}$  by Oyaro et al.<sup>5</sup>

The rate coefficient of  $k(\text{OH}+(\text{CF}_3)_2\text{CFOCH}_3) = (1.55 \pm 0.24) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  has been determined by Andersen et al.<sup>10</sup> This result together with the value of  $k_{12}$  determined in the present work shows that the substitution of the middle hydrogen atom in  $(\text{CF}_3)_2\text{CHOCH}_3$  by a fluorine atom to give  $(\text{CF}_3)_2\text{CFOCH}_3$  decreases the reactivity toward OH radicals by a factor of 12.

**3.3. Product Study of  $(\text{CF}_3)_2\text{CHOCH}_3 + \text{Cl}$ .** Smog chamber studies were conducted both at Ford and CCAR to study the mechanism of the Cl initiated oxidation of  $(\text{CF}_3)_2\text{CHOCH}_3$ . At Ford initial reactant mixtures consisted of 8.7–12.0 mTorr of  $(\text{CF}_3)_2\text{CHOCH}_3$ , 147.0–149.3 mTorr of  $\text{Cl}_2$ , 0–14.7 mTorr of NO, and 14.0–700 Torr of  $\text{O}_2$  made up to 700 Torr total pressure using  $\text{N}_2$ . At CCAR the initial reaction mixtures consisted of 3.03–3.4 mTorr of  $(\text{CF}_3)_2\text{CHOCH}_3$  and 66.2–119.9 mTorr of  $\text{Cl}_2$  in 700 Torr of air or  $\text{O}_2$ .

Figure 3 shows IR spectra of a mixture of 11.8 mTorr of  $(\text{CF}_3)_2\text{CHOCH}_3$ , 148 mTorr of  $\text{Cl}_2$ , and 14 Torr of  $\text{O}_2$  in 700

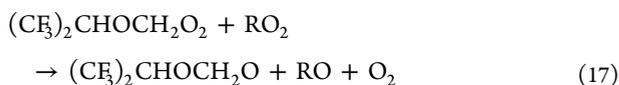


**Figure 3.** IR spectra before (panel A) and after (panel B) 15 s UV irradiation of a mixture of 11.8 mTorr of  $(\text{CF}_3)_2\text{CHOCH}_3$ , 148 mTorr of  $\text{Cl}_2$ , and 14 Torr of  $\text{O}_2$  in 700 Torr of  $\text{N}_2$ . Panel C is the residual spectrum obtained by subtracting  $0.68 \times$  panel A from panel B. We assign the spectrum shown in panel C to the formate  $(\text{CF}_3)_2\text{CHOCHO}$ , see text for details.

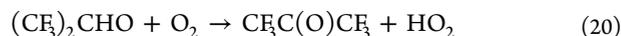
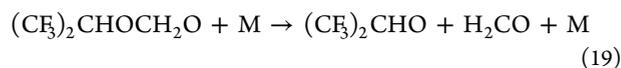
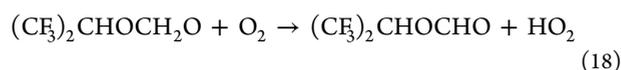
Torr total pressure with  $\text{N}_2$  diluent before (panel A) and after (panel B) 15 s of UV irradiation. The residual spectrum in panel C was obtained by subtracting the features attributable to  $(\text{CF}_3)_2\text{CHOCH}_3$  from panel B; 32% of  $(\text{CF}_3)_2\text{CHOCH}_3$  was consumed during the UV irradiation. The reaction of  $(\text{CF}_3)_2\text{CHOCH}_3$  with Cl atoms can follow two pathways: hydrogen abstraction from the terminal carbon (the  $-\text{CH}_3$  group) or from the center carbon atom (the  $-\text{CH}-$  group).



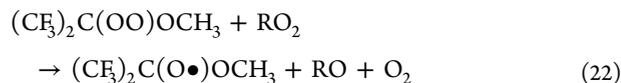
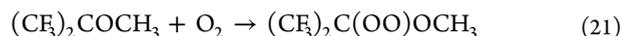
After hydrogen abstraction from the  $-\text{CH}_3$  group, reaction 9a, the alkyl radical will add  $\text{O}_2$  to give a peroxy radical, which will react with other peroxy radicals ( $\text{RO}_2$ ) to give an alkoxy radical.



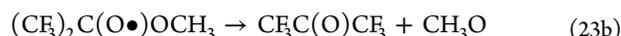
The alkoxy radical will either react with  $\text{O}_2$ , giving a formate, or decompose via C–C scission, giving a  $(\text{CF}_3)_2\text{CHO}$  radical and formaldehyde ( $\text{H}_2\text{CO}$ ). The  $(\text{CF}_3)_2\text{CHO}$  radical will react with  $\text{O}_2$  to give hexafluoroacetone:



Reaction 9b, with hydrogen abstraction from the  $-\text{CH}-$  group, yields an alkyl radical that reacts with  $\text{O}_2$  to form a peroxy radical that is transformed into an alkoxy radical via reaction with another peroxy radical (or  $\text{NO}$ , if present):



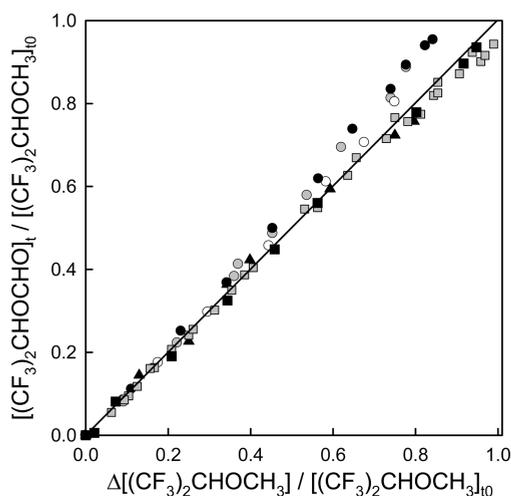
The alkoxy radical formed in reaction 22 can decompose to form the ester  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  and a  $\text{CF}_3$  radical, or hexafluoroacetone ( $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ ) and a  $\text{CH}_3\text{O}$  radical:



The  $\text{CF}_3$  radical will react with  $\text{O}_2$  to form  $\text{CF}_3\text{O}_2$  radicals, which will react further and eventually give  $\text{C}(\text{O})\text{F}_2$ .<sup>22</sup> No formation of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  or  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  was observed; upper limits for the molar yields of these products were 2.1% and 0.7%. We conclude that reaction pathway 9b is not important and that unimolecular decomposition via reaction 19 is not significant. The residual spectrum in panel C is assigned to the formate  $(\text{CF}_3)_2\text{CHOCHO}$ . The carbonyl ( $\text{C}=\text{O}$ ) stretching feature at  $1778 \text{ cm}^{-1}$  and the other features in Figure 3 panel C scaled linearly with the loss of  $(\text{CF}_3)_2\text{CHOCH}_3$ .  $(\text{CF}_3)_2\text{CHOCHO}$  is the sole product of the Cl-atom initiated oxidation of  $(\text{CF}_3)_2\text{CHOCH}_3$ .

In contrast to the present findings, Oyaro et al.<sup>5</sup> reported the ester  $(\text{CF}_3\text{C}(\text{O})\text{OCH}_3)$  to be the main product of the Cl atom initiated atmospheric oxidation of  $(\text{CF}_3)_2\text{CHOCH}_3$  in a yield of >99% with the formate being a minor product. We searched for features attributable to  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  in the product spectra in experiments conducted at Ford and CCAR; none were found, and we derived an upper limit of 2.1% for this product. Our finding that  $(\text{CF}_3)_2\text{CHOCHO}$  is the only observable product of the Cl atom initiated reaction is based on experiments conducted in two laboratories using a range of  $\text{O}_2$  partial pressures, both in the presence and in the absence of  $\text{NO}$ . As seen in Figure 4, there was no discernible dependence on the  $\text{O}_2$  partial pressure or the presence of  $\text{NO}$  on the observed yield of  $(\text{CF}_3)_2\text{CHOCHO}$ . Oyaro et al. used GC–MS in their analysis. This is a sensitive analytical technique. However, it appears that Oyaro et al. misidentified the major product ion.

Our results for  $(\text{CF}_3)_2\text{CHOCH}_3$  are consistent with previous studies of the degradation of HFEs with the general formulas  $\text{C}_x\text{F}_{2x+1}\text{OCH}_3$  and  $\text{C}_x\text{F}_{2x+1}\text{CH}_2\text{OCH}_3$  which are converted into the corresponding formates,  $\text{C}_x\text{F}_{2x+1}\text{OCHO}$  and  $\text{C}_x\text{F}_{2x+1}\text{CH}_2\text{OCHO}$ .<sup>7–9,11,23</sup> The product study shows that the reaction of chlorine atoms with  $(\text{CF}_3)_2\text{CHOCH}_3$  proceeds mainly, if not exclusively, via H atom abstraction from the  $-\text{CH}_3$  group. The fact that  $(\text{CF}_3)_2\text{CFOCH}_3$  is 30 times less reactive than  $(\text{CF}_3)_2\text{CHOCH}_3$  toward Cl atoms (see section 3.1) reflects a deactivation by the additional fluorine atom of



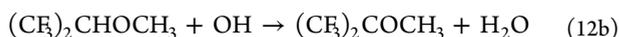
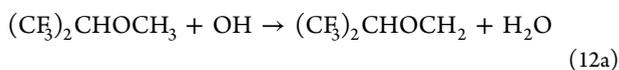
**Figure 4.** Plot of observed concentration of  $(\text{CF}_3)_2\text{CHOCHO}$  normalized to the initial  $(\text{CF}_3)_2\text{CHOCH}_3$  concentration versus the fractional loss of  $(\text{CF}_3)_2\text{CHOCH}_3$  following irradiation of  $(\text{CF}_3)_2\text{CHOCH}_3$  and  $\text{Cl}_2$  in 700 Torr of  $\text{N}_2/\text{O}_2$  mixtures in the presence (triangles) or absence (circles/squares) of  $\text{NO}$ . The  $\text{O}_2$  partial pressures were 14 Torr (open symbols), 140 Torr (gray symbols), and 700 Torr (solid symbols). The data from CCAR are square symbols, and the data from Ford are circles and triangles. The line is a linear fit.

the C–H bonds in the  $-\text{CH}_3$  group. The deactivation presumably is attributable to the inductive effect of the C–F bond which strengthens the C–H bonds.

By analogy to other fluorinated formates, uptake into cloud, rain, seawater, and hydrolysis on a time scale of months is probably a significant atmospheric fate of the formate  $(\text{CF}_3)_2\text{CHOCHO}$ .<sup>24,25</sup> The formate can also react with Cl atoms or OH radicals and degrade further in the atmosphere; see sections 3.5 and 3.6.

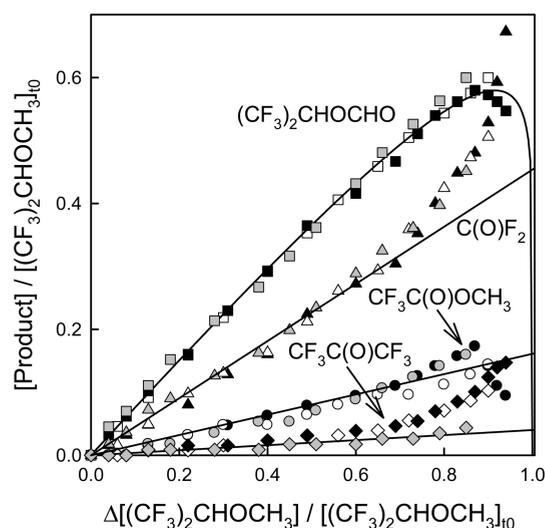
**3.4. Product Study of  $(\text{CF}_3)_2\text{CHOCH}_3 + \text{OH}$ .** Smog chamber studies were performed at CCAR to investigate the mechanism of the OH initiated oxidation of  $(\text{CF}_3)_2\text{CHOCH}_3$ . Initial reactant mixtures consisted of 3.0–3.3 mTorr of  $(\text{CF}_3)_2\text{CHOCH}_3$ , 1.5–2.7 Torr of  $\text{O}_3$ , and 275–379 mTorr of  $\text{H}_2$  with 0–200 Torr of  $\text{O}_2$  at a total pressure of 200 Torr made up with  $\text{N}_2$  diluent. One experiment was performed in 700 Torr total pressure of air.

As for Cl atoms, the reaction of OH radicals with  $(\text{CF}_3)_2\text{CHOCH}_3$  can proceed at the two different reaction sites giving two alkyl radicals:



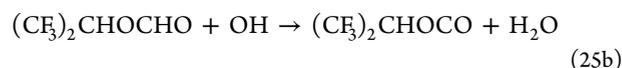
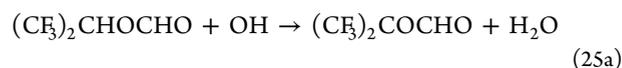
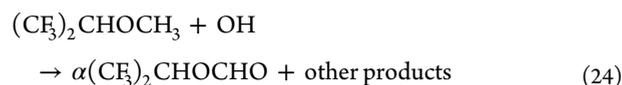
The alkyl radicals generated in reactions 12a and 12b will react with  $\text{O}_2$  and decompose following the reactions outlined earlier (see section 3.3).

Figure 5 shows the yields of the products obtained for a range of oxygen partial pressures. In contrast to the Cl initiated oxidation of  $(\text{CF}_3)_2\text{CHOCH}_3$ , the OH initiated oxidation proceeds via H abstraction from both the terminal and the central reaction sites. As seen from Figure 5, there was no discernible effect of  $\text{O}_2$  partial pressure on the product yields. The nonlinear fit to the  $(\text{CF}_3)_2\text{CHOCHO}$  data in Figure 5 as derived by Meagher et al.<sup>26</sup> describes the conversion of



**Figure 5.** Plot of observed concentration of  $(\text{CF}_3)_2\text{CHOCHO}$  (squares),  $\text{C}(\text{O})\text{F}_2$  (triangles),  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  (circles), and  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  (diamonds), normalized to the initial  $(\text{CF}_3)_2\text{CHOCH}_3$  concentration, versus the fractional loss of  $(\text{CF}_3)_2\text{CHOCH}_3$  following irradiation of a mixture of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $\text{H}_2$ , and  $\text{O}_3$  in 200 Torr of air (open symbols), 200 Torr of  $\text{O}_2$  (gray symbols), and 700 Torr of air (solid symbols). The lines are fits to the data; see text for details.

$(\text{CF}_3)_2\text{CHOCH}_3$  to  $(\text{CF}_3)_2\text{CHOCHO}$  as a function of the fractional loss of the ether using two parameters: the formate yield ( $\alpha$ ) and the rate coefficient ratio  $k_{25}/k_{24}$ .



The equation for the fit is

$$\frac{[(\text{CF}_3)_2\text{CHOCHO}]_t}{[(\text{CF}_3)_2\text{CHOCH}_3]_0} = \frac{\alpha}{1 - \frac{k_{25}}{k_{24}}} (1 - x) \{ (1 - x)^{(k_{25}/k_{24} - 1)} - 1 \} \quad (II)$$

where  $x$  is the fractional conversion of the formate  $(\text{CF}_3)_2\text{CHOCHO}$ :

$$x \equiv 1 - \frac{[(\text{CF}_3)_2\text{CHOCHO}]_t}{[(\text{CF}_3)_2\text{CHOCH}_3]_0} \quad (III)$$

The fit of eq II to the formate data in Figure 5 gives  $\alpha = (76 \pm 8)\%$  and  $k_{25}/k_{24} = (0.11 \pm 0.02)$ . The nonlinear fit to the  $(\text{CF}_3)_2\text{CHOCHO}$  data shown in Figure 5 provides an estimate of the rate coefficient of the reaction of  $(\text{CF}_3)_2\text{CHOCHO}$  with OH radicals from the rate coefficient ratio  $k_{25}/k_{24}$ . Using  $k_{24}(\text{OH} + (\text{CF}_3)_2\text{CHOCH}_3) = (1.86 \pm 0.41) \times 10^{-13}$  determined above we derive  $k_{25}(\text{OH} + (\text{CF}_3)_2\text{CHOCHO}) = (2.08 \pm 0.63) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The reactivity of  $(\text{CF}_3)_2\text{CHOCHO}$  is indistinguishable from that of  $\text{CF}_3\text{OCHO}$ :  $k(\text{OH} + \text{CF}_3\text{OCHO}) = (1.68 \pm 0.20) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  determined by Chen et al.,<sup>27</sup> suggesting that the majority of

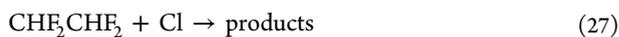
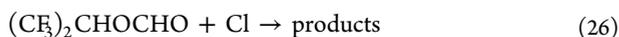
reaction occurs via attack at the formyl C–H bond (reaction 25b).

Linear fits to the initial data shown in Figure 5 give product yields of  $(16 \pm 2)\%$ ,  $(4 \pm 1)\%$ , and  $(45 \pm 5)\%$  for  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ ,  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ , and  $\text{C}(\text{O})\text{F}_2$  respectively. These results are consistent with those reported by Chen et al.<sup>6</sup> who identified four products:  $(\text{CF}_3)_2\text{CHOCHO}$ ,  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ ,  $\text{CF}_3\text{C}(\text{OH})_2\text{CF}_3$ , and  $\text{C}(\text{O})\text{F}_2$  in yields of  $(66 \pm 11)\%$ ,  $(22 \pm 2)\%$ ,  $(4 \pm 5)\%$ , and  $(33 \pm 2)\%$ , respectively. Chen et al.<sup>6</sup> conducted their experiments in the presence of water;  $\text{CF}_3\text{C}(\text{OH})_2\text{CF}_3$  is formed by reaction of  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  with water so the yield of  $\text{CF}_3\text{C}(\text{OH})_2\text{CF}_3$  from Chen et al. should be compared to that of  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  in this study. The combined yield of  $(\text{CF}_3)_2\text{CHOCHO}$ ,  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ , and  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  accounts for the loss of  $(\text{CF}_3)_2\text{CHOCH}_3$ . Based on the  $(\text{CF}_3)_2\text{CHOCHO}$  yield and the combined  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  and  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  yield, the reaction of OH radicals with  $(\text{CF}_3)_2\text{CHOCH}_3$  proceeds  $(76 \pm 8)\%$  via channel 12a and  $(20 \pm 4)\%$  via channel 12b. This is contrary to the findings by Oyaro et al.,<sup>5</sup> who report  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  as the main product and  $(\text{CF}_3)_2\text{CHOCHO}$  as the minor product of the OH-radical initiated oxidation. Furthermore, they do not see a difference in the products between the Cl atom and OH radical oxidations. We cannot explain why Oyaro et al. did not observe a difference in the product distributions between OH radical and Cl atom initiated oxidation of  $(\text{CF}_3)_2\text{CHOCH}_3$ . The results from our study confirm the findings by Chen et al.<sup>6</sup>

The fact that products originating from the oxidation pathway following reaction 12b were observed in the OH product study shows that OH radicals are less selective than Cl atoms in their reaction with  $(\text{CF}_3)_2\text{CHOCH}_3$ . The H–Cl bond is weaker than the H–OH bond:  $432 \text{ kJ mol}^{-1}$  versus  $497 \text{ kJ mol}^{-1}$ . A likely explanation for the greater selectivity of Cl atoms is that the inductive effect of the  $-\text{CF}_3$  groups increases the tertiary C–H bond energy close to, or above,  $432 \text{ kJ mol}^{-1}$ . For C–H bond energies greater than  $432 \text{ kJ mol}^{-1}$  the Cl atom reaction would be endothermic and would cease to be important. In contrast, the OH radical reaction would still be exothermic and hence less sensitive to changes in the C–H bond energy. Thomsen et al.<sup>9</sup> and Østerstrøm et al.<sup>8</sup> have shown that Cl atoms are more selective than OH radicals in their reactions with  $\text{C}_2\text{F}_5\text{CH}_2\text{OCH}_3$  and  $\text{CF}_3\text{CH}_2\text{OCH}_3$ . In the present work we do not observe any evidence for reaction of Cl atoms at the tertiary C–H bond in  $(\text{CF}_3)_2\text{CHOCH}_3$ , suggesting that this C–H bond has a strength of  $432 \text{ kJ mol}^{-1}$ , or greater, preventing hydrogen abstraction by Cl atoms.

### 3.5. Relative Rate Study of $(\text{CF}_3)_2\text{CHOCHO} + \text{Cl}$ .

Relative rate experiments were performed at CCAR to study the kinetics of the reaction of Cl atoms with  $(\text{CF}_3)_2\text{CHOCHO}$ . In these experiments all of the starting reactant compound,  $(\text{CF}_3)_2\text{CHOCH}_3$ , was allowed to react with Cl atoms generating  $(\text{CF}_3)_2\text{CHOCHO}$ . Then either  $\text{CHF}_2\text{CHF}_2$  or  $\text{CD}_4$  was added and the rate of reaction 26 was monitored relative to reactions 27 and 28. Initial reactant mixtures consisted of 3.13–3.23 mTorr of  $(\text{CF}_3)_2\text{CHOCH}_3$ , 161.2–174.9 mTorr of  $\text{Cl}_2$ , and either 5.32–10.5 mTorr of  $\text{CHF}_2\text{CHF}_2$  or 5.21 mTorr of  $\text{CD}_4$ , in 700 Torr of air. These mixtures allowed for generation of peak  $(\text{CF}_3)_2\text{CHOCHO}$  concentrations of 1.34–1.64 mTorr.



The observed loss of  $(\text{CF}_3)_2\text{CHOCHO}$  versus the reference compounds in the presence of Cl atoms is shown in Figure 6.

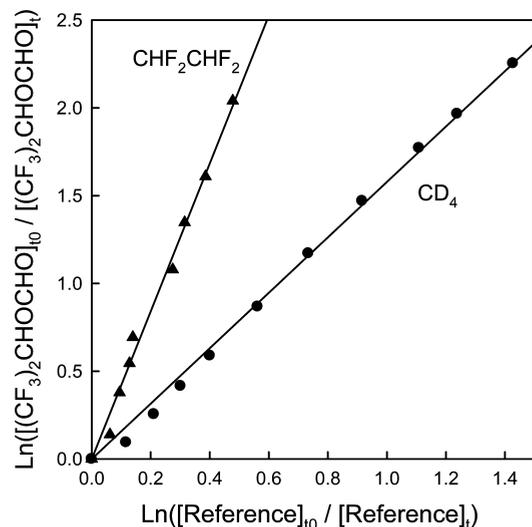


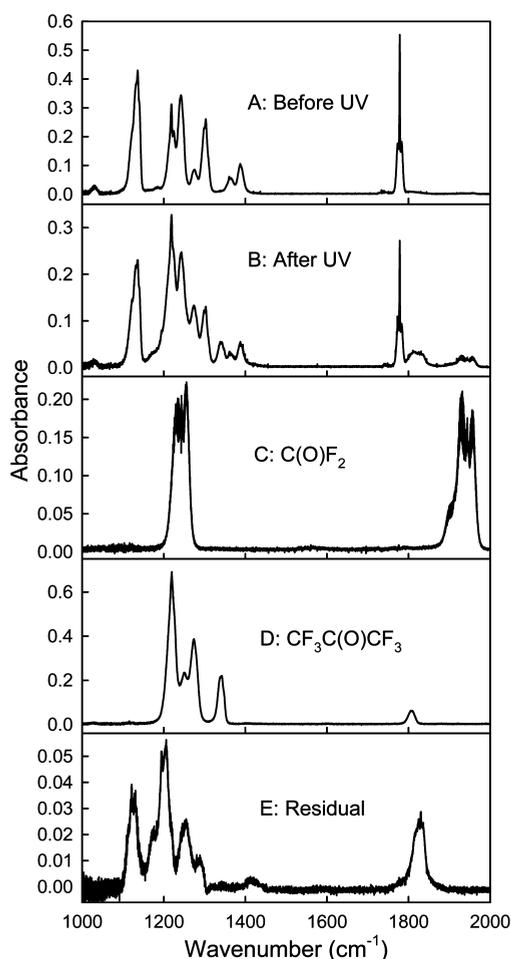
Figure 6. Decay of  $(\text{CF}_3)_2\text{CHOCHO}$  versus  $\text{CHF}_2\text{CHF}_2$  (triangles) and  $\text{CD}_4$  (circles) in the presence of Cl atoms in 700 Torr of air.

Linear least-squares analysis of the data in Figure 6 gives  $k_{26}/k_{27} = (4.21 \pm 0.45)$  and  $k_{26}/k_{28} = (1.58 \pm 0.16)$ . Using  $k_{27}(\text{Cl} + \text{CHF}_2\text{CHF}_2) = (2.2 \pm 0.2) \times 10^{-15} \text{ s}^{-1}$ <sup>28</sup> and  $k_{28}(\text{Cl} + \text{CD}_4) = (6.09 \pm 0.48) \times 10^{-15} \text{ s}^{-1}$ <sup>29</sup> gives  $k_{26}(\text{Cl} + (\text{CF}_3)_2\text{CHOCHO}) = (9.26 \pm 1.31) \times 10^{-15}$  and  $(9.61 \pm 1.24) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The values of  $k_{26}$  obtained using the two different references were indistinguishable, suggesting the absence of significant systematic errors. We choose to report a final value which is the average of the individual determinations with error limits which encompass the extremes of the determinations, yielding  $k_{26}(\text{Cl} + (\text{CF}_3)_2\text{CHOCHO}) = (9.44 \pm 1.81) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Andersen et al.<sup>10</sup> and Ninomiya et al.<sup>11</sup> have determined  $k(\text{Cl} + (\text{CF}_3)_2\text{CFOCHO}) = (1.47 \pm 0.56) \times 10^{-14}$  and  $k(\text{Cl} + n\text{-C}_3\text{F}_7\text{OCHO}) = (8.2 \pm 2.2) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Our result for  $(\text{CF}_3)_2\text{CHOCHO}$  is indistinguishable from those for  $(\text{CF}_3)_2\text{CFOCHO}$  and  $n\text{-C}_3\text{F}_7\text{OCHO}$ . It is interesting to contrast the rate coefficient ratios  $k(\text{Cl} + (\text{CF}_3)_2\text{CHOCHO})/k(\text{Cl} + (\text{CF}_3)_2\text{CFOCHO}) \approx 1$  and  $k(\text{Cl} + (\text{CF}_3)_2\text{CHOCH}_3)/k(\text{Cl} + (\text{CF}_3)_2\text{CFOCH}_3) \approx 30$ . Computational studies would be of interest to understand why the additional fluorine substituent in  $(\text{CF}_3)_2\text{CFOCH}_3$  has such a large impact while the additional fluorine substituent in  $(\text{CF}_3)_2\text{CFOCHO}$  has no discernible impact on the reactivity of the molecule compared to  $(\text{CF}_3)_2\text{CHOCH}_3$  and  $(\text{CF}_3)_2\text{CHOCHO}$ , respectively.

**3.6. Product Study of  $(\text{CF}_3)_2\text{CHOCHO} + \text{Cl}$ .** Product studies of the reaction of  $(\text{CF}_3)_2\text{CHOCHO}$  with Cl atoms were performed using the CCAR chamber following the same procedure as in section 3.5. All the starting reactant compound,  $(\text{CF}_3)_2\text{CHOCH}_3$ , was allowed to react with Cl atoms generating  $(\text{CF}_3)_2\text{CHOCHO}$ . Only then was the product formation monitored and normalized to the measured decay of  $(\text{CF}_3)_2\text{CHOCHO}$ . Initial reactant concentrations were 3.13–3.18 mTorr of  $(\text{CF}_3)_2\text{CHOCH}_3$ , 142.4–192.1 mTorr of  $\text{Cl}_2$ , and 140–700 Torr of  $\text{O}_2$  at a total pressure of 700 Torr made up with  $\text{N}_2$ . These mixtures allowed for the generation of peak  $(\text{CF}_3)_2\text{CHOCHO}$  concentrations of 1.12–1.44 mTorr.

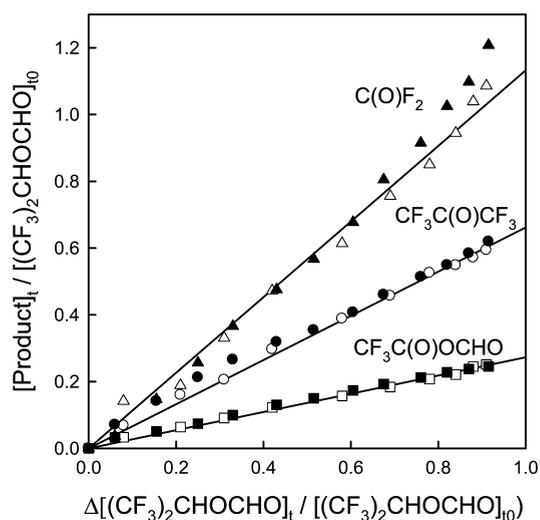
Figure 7 shows IR spectra of a typical reaction mixture of  $(\text{CF}_3)_2\text{CHOCHO}$  and  $\text{Cl}_2$  in 700 Torr of  $\text{O}_2$  diluent before



**Figure 7.** IR spectra before (panel A) and after (panel B) a 130 s UV irradiation of a mixture of  $(\text{CF}_3)_2\text{CHOCHO}$  and  $\text{Cl}_2$  in 700 Torr of  $\text{O}_2$ . Panels C and D are reference spectra of  $\text{C}(\text{O})\text{F}_2$  and  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ . Panel E is the residual spectrum generated by subtraction of features attributable to  $(\text{CF}_3)_2\text{CHOCHO}$  ( $0.48 \times$  panel A),  $\text{C}(\text{O})\text{F}_2$ , and  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  from panel B. The spectrum in panel E is attributed to  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$ ; see text for details.

(panel A) and after (panel B) 130 s of UV irradiation, and reference spectra of  $\text{C}(\text{O})\text{F}_2$  (panel C) and  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  (panel D). The residual spectrum in panel E was obtained by subtracting features attributable to  $(\text{CF}_3)_2\text{CHOCHO}$  ( $0.48 \times$  panel A),  $\text{C}(\text{O})\text{F}_2$ , and  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  from panel B. The carbonyl ( $\text{C}=\text{O}$ ) features at 1825 and 1830  $\text{cm}^{-1}$  and other features in the residual scaled linearly with consumption of the formate, and we assign the residual to  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$ . The IR spectrum of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  was calculated using density functional theory (DFT) with Gaussian 09<sup>30</sup> at the B3LYP/6-31+G(d,p) level and is given in the [Supporting Information](#). In [Figure 8](#) we assume that  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  accounts for the balance of  $(\text{CF}_3)_2\text{CHOCHO}$  loss not accounted for by  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ .

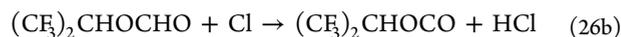
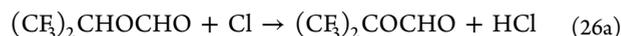
[Figure 8](#) shows plots of the formation of  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ ,  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$ , and  $\text{C}(\text{O})\text{F}_2$  versus the decay of  $(\text{CF}_3)_2\text{CHOCHO}$ . Linear regressions to the data in [Figure 8](#) give molar product yields for  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  and  $\text{COF}_2$  of  $(67 \pm 7)\%$  and  $(118 \pm 12)\%$ . Changes in  $\text{O}_2$  partial pressure over the



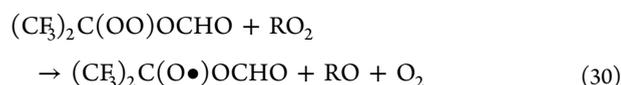
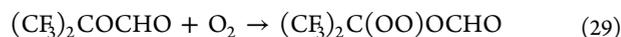
**Figure 8.** Plot of the observed concentration of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  (squares),  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  (circles), and  $\text{C}(\text{O})\text{F}_2$  (triangles) normalized to the initial  $(\text{CF}_3)_2\text{CHOCHO}$  concentration versus the fractional loss of  $(\text{CF}_3)_2\text{CHOCHO}$  following irradiation of mixtures containing  $(\text{CF}_3)_2\text{CHOCHO}$  and  $\text{Cl}_2$  in 700 Torr of either  $\text{O}_2$  (solid symbols) or air (open symbols).

range 140–700 Torr had no discernible effect on the product distribution.

The  $\text{Cl}$  initiated degradation of the formate follows a similar path to that described above for the ether.



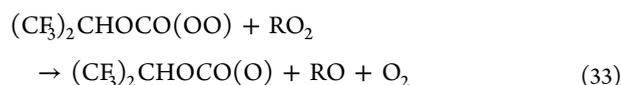
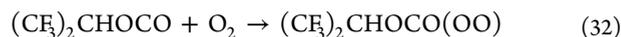
The alkyl radical generated in [reaction 26a](#) will react with  $\text{O}_2$  to form a peroxy radical, which can react with other peroxy radicals yielding an alkoxy radical.



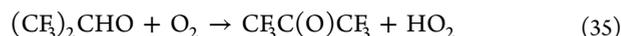
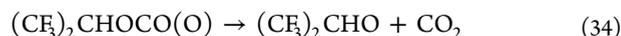
The alkoxy radical,  $(\text{CF}_3)_2\text{C}(\text{O}\bullet)\text{OCHO}$ , will undergo thermal decomposition yielding  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  and a  $\text{CF}_3$  radical.



The  $\text{CF}_3$  radical will react further, eventually yielding  $\text{C}(\text{O})\text{F}_2$ . The  $(\text{CF}_3)_2\text{CHOCO}$  radical generated in [reaction 26b](#) will react with  $\text{O}_2$ , forming a peroxy radical that subsequently is transformed into an alkoxy radical:

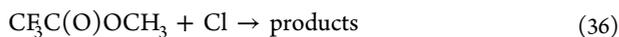


The alkoxy radical,  $(\text{CF}_3)_2\text{CHOCO}(\text{O})$ , will undergo  $\text{C}-\text{O}$  bond scission to yield  $\text{CO}_2$  and  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ :

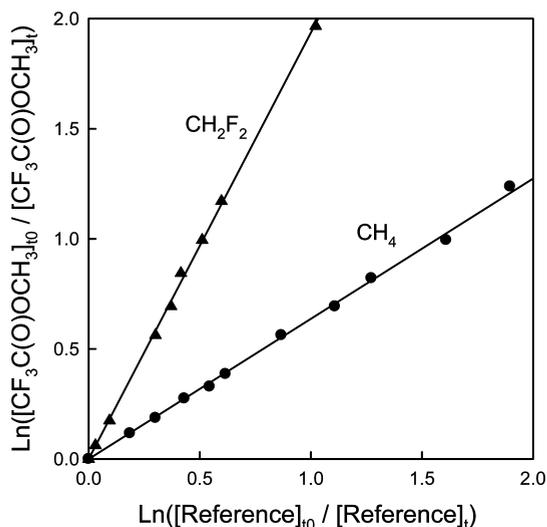


The observation of  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  and  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  during the Cl initiated degradation of  $(\text{CF}_3)_2\text{CHOCHO}$  shows that reaction channels 26a and 26b are both significant with  $(67 \pm 7)\%$  of the reaction proceeding via 26a and the balance via 26b.

**3.7. Relative Rate Study of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3 + \text{Cl}$ .** Relative rate studies were performed at CCAR to study the reaction of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  with Cl atoms. The initial reactant mixtures consisted of 3.02–3.13 mTorr of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ , 104–105 mTorr of  $\text{Cl}_2$ , and either 11.4 mTorr of  $\text{CH}_2\text{F}_2$  or 10.5 mTorr of  $\text{CH}_4$  in a total pressure of 700 Torr of  $\text{N}_2$ . Reaction 36 was measured relative to reactions 37 and 38:



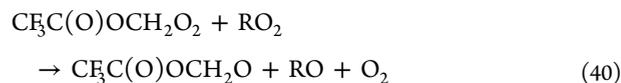
In Figure 9 the observed loss of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  versus the two reference compounds in the presence of Cl atoms is



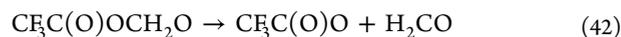
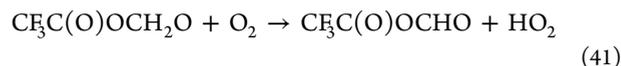
**Figure 9.** Decay of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  versus the reference compounds  $\text{CH}_2\text{F}_2$  (triangles) and  $\text{CH}_4$  (circles) in the presence of Cl atoms in 700 Torr of  $\text{N}_2$ .

shown. From the slopes of the linear least-squares analysis the rate coefficient ratios are found to be  $k_{36}/k_{37} = (1.94 \pm 0.20)$  and  $k_{36}/k_{38} = (0.64 \pm 0.06)$ . Using  $k_{37}(\text{Cl}+\text{CH}_2\text{F}_2) = (3.2 \pm 0.5) \times 10^{-14} \text{ s}^{-1}$  and  $k_{38}(\text{Cl}+\text{CH}_4) = (1.0 \pm 0.06) \times 10^{-13} \text{ s}^{-1}$  gives  $k_{36}(\text{Cl}+\text{CF}_3\text{C}(\text{O})\text{OCH}_3) = (6.20 \pm 0.63) \times 10^{-14}$  and  $(6.37 \pm 0.75) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We choose to report a final rate coefficient, which is the average of the two determinations with uncertainties that encompass the extremes of the determinations:  $k_{36}(\text{Cl}+\text{CF}_3\text{C}(\text{O})\text{OCH}_3) = (6.28 \pm 0.98) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Blanco et al. have reported  $k_{36}(\text{Cl}+\text{CF}_3\text{C}(\text{O})\text{OCH}_3) = (9.0 \pm 3.0) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>32</sup> consistent with the value measured here.

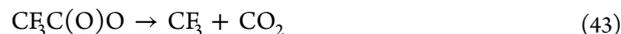
**3.8. Product Study of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3 + \text{Cl}$ .** The products of the Cl-atom initiated oxidation of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  were studied using the CCAR photoreactor. The initial reactant mixtures consisted of 2.73–3.80 mTorr of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ , 72.4–141 mTorr of  $\text{Cl}_2$ , and 17–700 Torr of  $\text{O}_2$  in a total pressure of 700 Torr made up with  $\text{N}_2$  diluent. The degradation of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  leads to the formation of an alkoxy radical (RO):



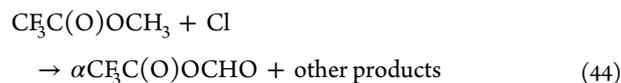
The alkoxy radical can either react with  $\text{O}_2$  or decompose via C–C scission:



The radical  $\text{CF}_3\text{C}(\text{O})\text{O}$  will decompose into a  $\text{CF}_3$  radical and  $\text{CO}_2$ :



The  $\text{CF}_3$  radical will react with  $\text{O}_2$  to give  $\text{CF}_3\text{O}_2$  radicals, which react further to give  $\text{CF}_3\text{O}$  radicals, which will eventually yield  $\text{C}(\text{O})\text{F}_2$ . Figure 10 shows IR spectra of a mixture of 2.73 mTorr of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  and 139.7 mTorr of  $\text{Cl}_2$  in 700 Torr of  $\text{O}_2$  before (panel A) and after (panel B) 140 s of UV irradiation. Panels C and D show reference spectra of  $\text{C}(\text{O})\text{F}_2$  and  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$ . The residual spectrum in panel E was obtained by subtracting features of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  ( $0.47 \times$  panel A),  $\text{C}(\text{O})\text{F}_2$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  from panel B. The observed products are  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  and  $\text{C}(\text{O})\text{F}_2$ . As seen from Figure 11, increasing the  $\text{O}_2$  partial pressure leads to an increase in the yield of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$ , indicating that there is a competition between reactions 41 and 42 for the available  $\text{CF}_3\text{C}(\text{O})\text{OCH}_2\text{O}$  radicals. No significant change in the yield of  $\text{C}(\text{O})\text{F}_2$  was observed, which suggests that the residual is formed in a competition with reactions 41 and 42, but faster than the formation of  $\text{C}(\text{O})\text{F}_2$  with increasing  $\text{O}_2$  partial pressure. The yield of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  at an  $\text{O}_2$  partial pressure of 17 Torr (white squares) from a linear regression to the data shown in Figure 11 is  $(40.8 \pm 4.1)\%$ . The two nonlinear fits in Figure 11 were obtained using the expression described by Meagher et al.<sup>26</sup> The formation and loss of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  can be summarized by reactions 44 and 45:



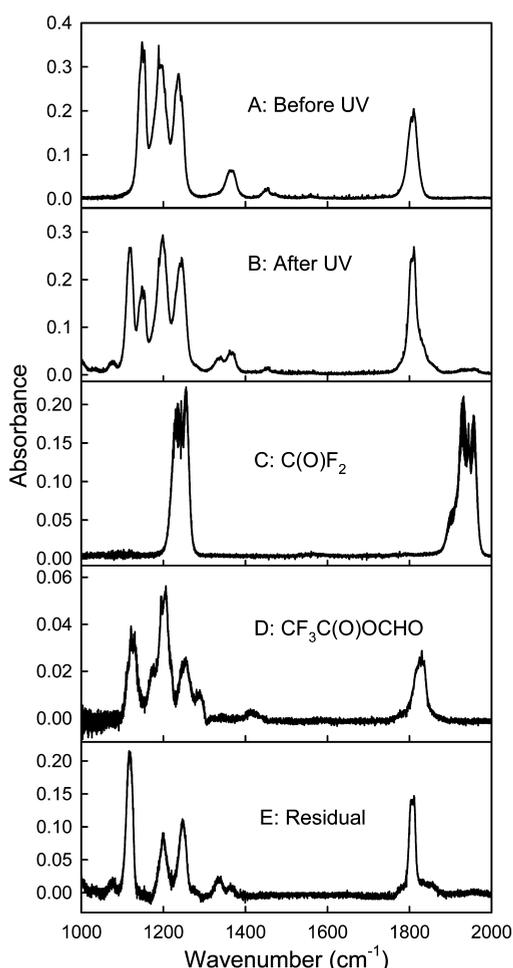
Here  $\alpha$  is the yield of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$ . The rate coefficient of reaction 44 is the same as for reaction 36 determined above.



The Meagher et al. fit describes the concentration of formation of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  in terms of its yield ( $\alpha$ ) in reaction 44, the rate coefficient ratio  $k_{45}/k_{44}$ , and the fractional loss of the ester  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  ( $x$ ). The expression for the fit is shown in eq IV for  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$ :

$$\begin{aligned} \frac{[\text{CF}_3\text{C}(\text{O})\text{OCHO}]_t}{[\text{CF}_3\text{C}(\text{O})\text{OCH}_3]_{t_0}} \\ = \frac{\alpha}{1 - \frac{k_{45}}{k_{44}}} (1 - x) \{ (1 - x)^{(k_{45}/k_{44} - 1)} - 1 \} \end{aligned} \quad (IV)$$

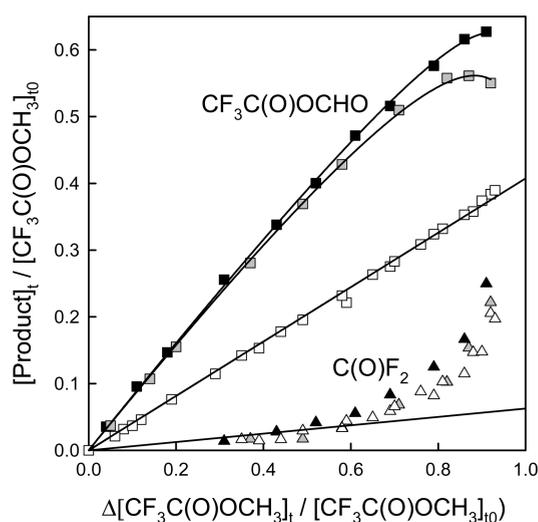
where  $x$  is defined as



**Figure 10.** IR spectra before (panel A) and after (panel B) a 140 s UV irradiation of a mixture of 2.73 mTorr of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  and 139.7 mTorr of  $\text{Cl}_2$  in 700 Torr of  $\text{O}_2$ . Panel C is a reference spectrum of  $\text{C}(\text{O})\text{F}_2$ . Panel D is the residual spectrum from Figure 7, used as a reference spectrum of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$ . Panel E is the residual spectrum after features attributable to  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  ( $0.47 \times$  panel A),  $\text{C}(\text{O})\text{F}_2$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  have been subtracted from panel B. The resulting spectrum has not been assigned; see text for details.

$$x \equiv 1 - \frac{[\text{CF}_3\text{C}(\text{O})\text{OCH}_3]_t}{[\text{CF}_3\text{C}(\text{O})\text{OCH}_3]_{t_0}} \quad (\text{V})$$

At  $\text{O}_2$  partial pressures of 140 and 700 Torr the nonlinear fits give the yields of  $(80.4 \pm 8.1)\%$  and  $(81.2 \pm 8.2)\%$  for  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  with 140 and 700 Torr of  $\text{O}_2$  partial pressure, respectively. With this range of  $\text{O}_2$  partial pressure the  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  yields are indistinguishable within the ranges of uncertainty. The yield of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  in air is the most relevant to the atmosphere and is quoted as the final yield of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  of  $(80.4 \pm 8.1)\%$ . It was observed that, when the  $\text{O}_2$  partial pressure is 17 Torr, the yield of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  is half the yield of that obtained with an  $\text{O}_2$  partial pressure of 140–700 Torr. This is to be expected since the formation of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  is due to reaction of the alkoxy radical  $\text{CF}_3\text{C}(\text{O})\text{OCH}_2\text{O}$  with  $\text{O}_2$  as shown in reaction 42. From the slope of the linear regression of the initial  $\text{C}(\text{O})\text{F}_2$  data in Figure 11, a maximum initial yield of  $\text{C}(\text{O})\text{F}_2$  from reaction of the  $\text{CF}_3$  radical formed in reaction 43 and secondarily from the decomposition of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  has been estimated to be  $(6.3 \pm 1.1)\%$ . The residual shown in panel E of Figure 10 is an



**Figure 11.** Plot of the observed concentration of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  (squares) and  $\text{C}(\text{O})\text{F}_2$  (triangles) normalized to the initial concentration of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  versus the fractional loss of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  following UV irradiation of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3/\text{Cl}_2$  mixtures in 700 Torr of  $\text{O}_2/\text{N}_2$ . The  $\text{O}_2$  partial pressures were 17 Torr (open symbols), 140 Torr (gray symbols), and 700 Torr (solid symbols). The lines are fits to the data; see text for details.

unidentified product. The high intensity peak at  $1810 \text{ cm}^{-1}$  indicates a  $\text{C}=\text{O}$  stretch and scales as a function of reaction extent with the peak found at  $1120 \text{ cm}^{-1}$ . The compound is assumed to balance the mass of the ester degradation, therefore accounting for 4.1–22.5% of the ester loss within the ranges of uncertainty of the combined yields of  $\text{CF}_3\text{C}(\text{O})\text{OCHO}$  and  $\text{C}(\text{O})\text{F}_2$ . Seeing that bis(trifluoromethyl) trioxide,  $\text{CF}_3\text{O}_3\text{CF}_3$ , has been observed to form from the reaction of  $\text{CF}_3\text{O}$  and  $\text{CF}_3\text{O}_2$  radicals in the degradation of other fluorinated compounds,<sup>14,22,33,34</sup> the unknown residual was compared to a reference spectrum of  $\text{CF}_3\text{O}_3\text{CF}_3$  which was rejected as a possible product. A screening of different possible products with DFT methods using Gaussian 09<sup>30</sup> at the B3LYP/6-31+G(d,p) and WB97XD/cc-pVTZ levels suggests that  $\text{CF}_3\text{C}(\text{O})\text{OCH}_2\text{OH}$  (possible minor product of  $\text{R}_\text{H}\text{O}_2 + \text{RO}_2$  reactions) is the main contributor to the residual spectrum, but we were unable to positively assign the residual IR bands to confirm this. Optimized structures and IR spectra can be found in the Supporting Information. Further computational studies may aid in this regard, but that is beyond the scope of the present work.

**3.9. Atmospheric Lifetimes of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ .** Organic compounds are removed from the atmosphere via photolysis, wet and dry deposition, and reaction with  $\text{NO}_3$  radicals,  $\text{O}_3$ , OH radicals, and Cl atoms. The compounds studied in the present work,  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ , do not absorb UV light with wavelengths  $>200 \text{ nm}$ , so photolysis is not of importance.<sup>35</sup> The reactions with  $\text{NO}_3$  radicals and  $\text{O}_3$  are too slow to be of importance for saturated compounds such as  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ .<sup>36</sup>

The rate coefficients determined in this study can be used to estimate atmospheric lifetimes ( $\tau$ ) with respect to reaction with OH radicals and Cl atoms using the following equation:

$$\tau = \frac{1}{k_x \times [\text{X}]} \quad (\text{VI})$$

X is either OH radicals or Cl atoms. Assuming a global weighted-average OH concentration of  $1.0 \times 10^6 \text{ cm}^{-3}$ ,<sup>37</sup> and using the rate constants measured here and  $k(\text{OH} + \text{CF}_3\text{C}(\text{O})\text{OCH}_3) = (5.2 \pm 0.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>20</sup> the atmospheric lifetimes of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  with respect to reaction with OH radicals are estimated to be 62 days, 1.5 years, and 220 days, respectively. Assuming a global weighted-average Cl concentration of  $1.0 \times 10^3 \text{ cm}^{-3}$ ,<sup>38</sup> and using the rate coefficients measured here, the atmospheric lifetimes of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  with respect to reaction with Cl atoms are estimated to be 5.9, 3359, and 490 years, respectively. Clearly reaction with Cl atoms is not a significant fate for these compounds.

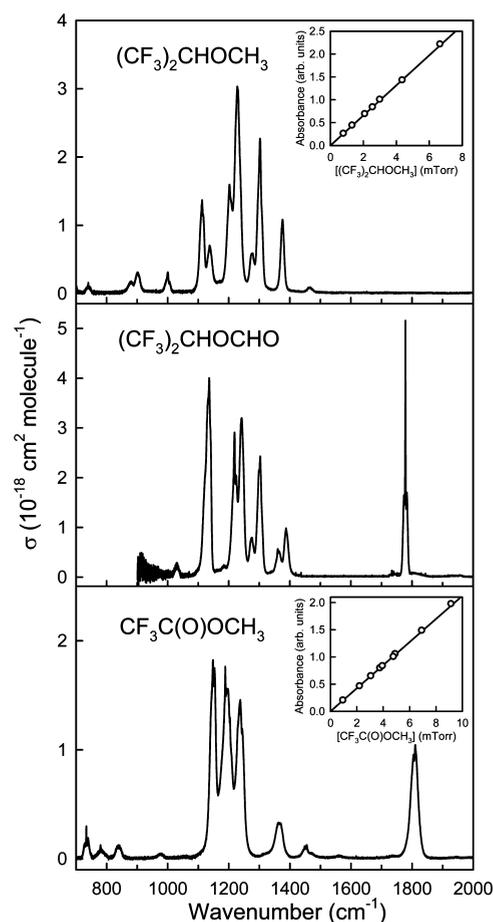
It is well established that species with Henry's law constants below approximately  $10^3 \text{ M atm}^{-1}$  partition strongly into the atmospheric gas phase.<sup>39</sup> Kutsuna et al. report a Henry's law constant for  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  of  $k_{\text{H}}(\text{CF}_3\text{C}(\text{O})\text{OCH}_3) = (0.12 \pm 0.04) \text{ M atm}^{-1}$ .<sup>40</sup> This indicates that the ester will mainly reside in the gas phase. Henry's law constants of  $(\text{CF}_3)_2\text{CHOCH}_3$  and  $(\text{CF}_3)_2\text{CHOCHO}$  have not been reported previously and are not included in the review by Sander,<sup>41</sup> but none of the similar fluorinated and oxygenated compounds in the study have Henry's law constants that suggest great partitioning of the compounds toward the aqueous phase in the atmosphere. Therefore, loss via wet deposition is unlikely to be the main sink for all three compounds. The carbonyl groups in  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  and  $(\text{CF}_3)_2\text{CHOCHO}$  make them more soluble in water than  $(\text{CF}_3)_2\text{CHOCH}_3$ , but based on the value of  $k_{\text{H}}(\text{CF}_3\text{C}(\text{O})\text{OCH}_3)$  the main atmospheric fate of the three compounds is most likely reaction with OH radicals. The lifetime estimates of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  with respect to reaction with OH radicals calculated above were used as the atmospheric lifetimes in the calculations below.

**3.10. IR Spectra and Global Warming Potentials of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ .** IR spectra of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  recorded in 700 Torr of air and  $296 \pm 2 \text{ K}$  at CCAR are shown in Figure 12. The integrated absorption cross sections are  $(\text{CF}_3)_2\text{CHOCH}_3$  ( $650\text{--}1500 \text{ cm}^{-1}$ ),  $2.44 \times 10^{-17}$ ;  $(\text{CF}_3)_2\text{CHOCHO}$  ( $1000\text{--}1800 \text{ cm}^{-1}$ ),  $3.24 \times 10^{-17}$ ; and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  ( $650\text{--}1900 \text{ cm}^{-1}$ ),  $1.71 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ . ASCII files of the spectra are included in the Supporting Information. Using the method described by Pinnock et al.,<sup>42</sup> radiative efficiencies for  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  of 0.291, 0.316, and  $0.244 \text{ W m}^{-2} \text{ ppb}^{-1}$  were calculated.

For compounds that are not well-mixed in the atmosphere a correction to the radiative forcing calculated using the Pinnock et al. method is needed. Hodnebrog et al.<sup>43</sup> provide the correction factor  $f(\tau)$  to the radiative efficiency based on the lifetime of the compound:

$$f(\tau) = \frac{a\tau^b}{1 + c\tau^d} \quad (\text{VII})$$

where  $a$ ,  $b$ ,  $c$ , and  $d$  are constants with values of 2.962, 0.9312, 2.994, and 0.9302, respectively. Using atmospheric lifetimes for  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  derived in this study, the correction factors are  $f(\tau) = 0.36$ , 0.81, and 0.65. The lifetime corrected radiative efficiencies of



**Figure 12.** IR spectra of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ . The insets show the calibration plots.

$(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  are 0.105, 0.255, and  $0.158 \text{ W m}^{-2} \text{ ppb}^{-1}$ , respectively.

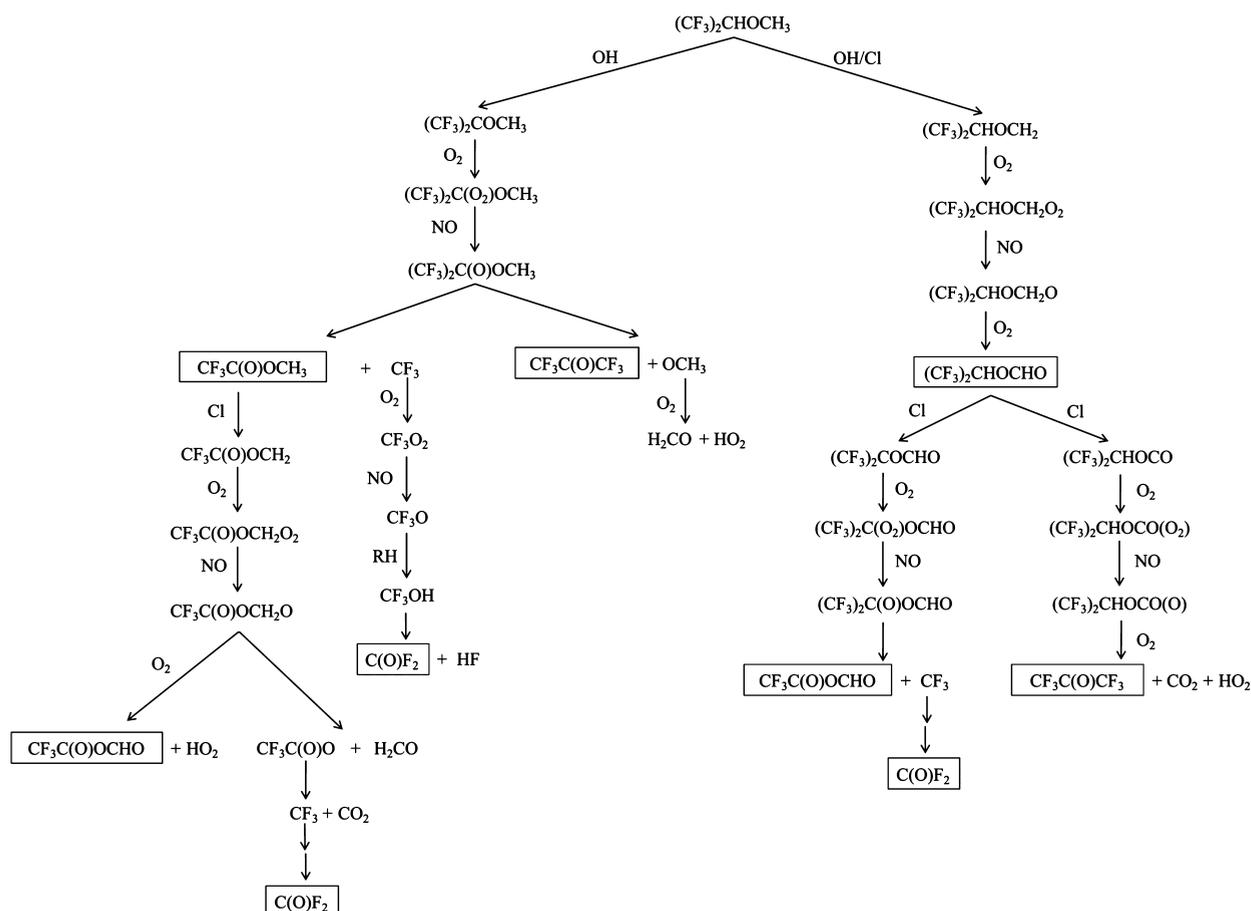
The global warming potential (GWP) is defined as the integrated radiative forcing over a given time horizon following the release of 1 kg of a compound compared to that for release of 1 kg of  $\text{CO}_2$ . The GWP for time horizon,  $t'$ , is defined as

$$\text{GWP}(x(t')) = \frac{\int_0^{t'} F_x \exp(-t/\tau_x) dt}{\int_0^{t'} F_{\text{CO}_2} R(t) dt} \quad (\text{VIII})$$

where  $F_{\text{CO}_2}$  is the radiative efficiency of  $\text{CO}_2$ ,  $R(t)$  is the response function that describes the decay of an instantaneous pulse of  $\text{CO}_2$ ,  $F_x$  is the radiative efficiency of compound  $x$ , and  $\tau_x$  is its atmospheric lifetime. The denominator in eq VIII is the absolute global warming potential (AGWP) for  $\text{CO}_2$ , which for 100 year time horizon is  $9.17 \times 10^{-14} \text{ W m}^{-2} \text{ yr kg}^{-1}$  (or  $0.722 \text{ W m}^{-2} \text{ yr ppm}^{-1}$ ).<sup>44</sup> The 100 year time horizon GWPs for  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  are estimated to be 6, 121, and 46, respectively.

#### 4. ATMOSPHERIC IMPACT

This work presents a comprehensive and self-consistent set of data concerning the atmospheric chemistry of  $(\text{CF}_3)_2\text{CHOCH}_3$ ,  $(\text{CF}_3)_2\text{CHOCHO}$ , and  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ . The OH radical and Cl atom kinetics of  $(\text{CF}_3)_2\text{CHOCH}_3$  and  $(\text{CF}_3)_2\text{CHOCHO}$  were determined, as well as the Cl atom kinetics of  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ . For  $(\text{CF}_3)_2\text{CHOCHO}$  no previous



**Figure 13.** Summary of the atmospheric degradation of  $(CF_3)_2CHOCH_3$  including the fate of the main products formed from the OH radical and Cl atom initiated degradation. Observed products are indicated by the boxes.

determinations of the OH and Cl rate coefficients have been reported. Studies of the Cl atom initiated oxidation of all three compounds and the OH radical initiated oxidation of  $(CF_3)_2CHOCH_3$  were conducted. The main features of the atmospheric degradation mechanism of  $(CF_3)_2CHOCH_3$  are given in Figure 13. We note that, in addition to the reaction of peroxy radicals with NO giving alkoxy radicals shown in Figure 13, peroxy radicals will react with  $HO_2$  radicals, with  $NO_2$ , and with other peroxy radicals. The reactions with  $HO_2$  radicals will give hydroperoxides (ROOH). The reactions with  $NO_2$  will give thermally unstable peroxy nitrates ( $ROONO_2$ ) which will decompose to regenerate the peroxy radicals and  $NO_2$ . Reactions with other peroxy radicals give alkoxy radicals, alcohols, and carbonyls.

The atmospheric lifetimes of  $(CF_3)_2CHOCH_3$  and its main oxidation product the formate  $(CF_3)_2CHOCHO$  with respect to reaction with OH radicals are estimated to be 62 days and 1.5 years. The atmospheric lifetime of  $CF_3C(O)OCH_3$  is estimated to be 220 days. GWPs of  $(CF_3)_2CHOCH_3$ ,  $(CF_3)_2CHOCHO$ , and  $CF_3C(O)OCH_3$  are estimated to be 6, 121, and 46, respectively.

$(CF_3)_2CHOCH_3$  does not contain chlorine and hence will not contribute to chlorine-catalyzed stratospheric ozone depletion. It has a short atmospheric lifetime and small GWP. The degradation products have longer atmospheric lifetimes than  $(CF_3)_2CHOCH_3$ , but still have  $GWP_{100}$  values below 150. None of the primary or secondary degradation products have any environmental impacts at the levels anticipated in the

environment due to oxidation of  $(CF_3)_2CHOCH_3$ . We conclude that the environmental impact of  $(CF_3)_2CHOCH_3$  is negligible.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b08204.

IR data and spectra (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank John Owens from 3M for supplying us with samples of  $(CF_3)_2CHOCH_3$  and  $CF_3C(O)OCH_3$ . We thank Henrik G. Kjaergaard for valuable discussions concerning the computational calculations of IR spectra. F.F.Ø. acknowledges financial support from Nordfluor and Oticon.

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