Atmospheric Chemistry of Pentachloroethane (CCl₃CCl₂H): Absorption Spectra of CCl₃CCl₂ and CCl₃CCl₂O₂ Radicals, Kinetics of the CCl₃CCl₂O₂ + NO Reaction, and Fate of the CCl₃CCl₂O Radical

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The absorption spectra of CCl₃CCl₂ and CCl₃CCl₂O₂ radicals and the rate constant for the reaction of CCl₃-CCl₂O₂ radicals with NO were measured at 296 \pm 2 K using a pulse radiolysis technique. The absorption spectra were measured over the wavelength range 220-400 nm. At 230 nm σ (CCl₃CCl₂) = (271 \pm 84) × 10⁻²⁰ cm² molecule⁻¹, and at 240 nm σ (CCl₃CCl₂O₂) = (145 \pm 21) × 10⁻²⁰ cm² molecule⁻¹. The reaction of F atoms with CCl₃CCl₂O₂ with NO proceeds with a rate constant of (2.3 \pm 1.6) × 10⁻¹² cm³ molecule⁻¹ s⁻¹. The reaction of CCl₃CCl₂O₂ with NO proceeds with a rate constant of (6.2 \pm 1.6) × 10⁻¹² cm³ molecule⁻¹ s⁻¹. This reaction gives NO₂ and CCl₃CCl₂O radicals. In the atmosphere, 85% of the CCl₃CCl₂O radicals eliminate a Cl atom to give CCl₃C(O)Cl, and the remaining 15% decompose via C-C bond scission to give CCl₃ radicals and COCl₂. As part of the present work, relative rate techniques were used to measure rate constants at 296 \pm 2 K for the reactions of Cl and F atoms with CCl₃CCl₂H of (5.2 \pm 0.7) × 10⁻¹⁴ and (2.0 \pm 0.5) × 10⁻¹² cm³ molecule⁻¹ s⁻¹, respectively.

1. Introduction

The adverse impact of chlorine released from chlorofluorocarbons (CFCs) on stratospheric ozone¹ has led to a ban on their production beginning in 1996. At this time a variety of compounds are being considered as CFC replacements. Hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) are two important classes of CFC replacements. The choice of HFCs and HCFCs is motivated by a number of considerations, not least of which is that, unlike CFCs, the HFCs and HCFCs contain at least one C-H bond which makes them susceptible to attack by OH radicals and, hence, to degradation in the troposphere.² The probable future economic importance of HFCs and HCFCs has generated considerable interest in their environmental acceptability and, thus, their atmospheric chemistry.² As a part of a collaborative study of the atmospheric chemistry of HFCs and HCFCs, we have undertaken an investigation of CCl₃CCl₂H. While CCl₃CCl₂H is not expected to assume any major industrial importance in the near future, it possesses structural similarity to some commercially important compounds, e.g., CF3CF2H and CF3CCl2H. Hence, information concerning CCl₃CCl₂H provides insight into the atmospheric chemistry of other more important compounds.

Following release into the atmosphere, CCl_3CCl_2H will react with OH radicals:

$$CCl_3CCl_2H + OH \rightarrow CCl_3CCl_2 + H_2O$$
(1)

The lifetime of CCl_3CCl_2H with respect to reaction with OH radicals is approximately 2.5 months.³ The CCl_3CCl_2 radical

The peroxy radical can react with NO, NO₂, HO₂, or other

peroxy radicals $\mathbf{R}'\mathbf{O}_2$:^{2.4,5}

formed in reaction 1 will react with O₂ to give a peroxy radical:

 $CCl_3CCl_2 + O_2 + M \rightarrow CCl_3CCl_2O_2 + M$

$$CCl_3CCl_2O_2 + NO \rightarrow CCl_3CCl_2O + NO_2$$
 (3)

(2)

$$CCl_3CCl_2O_2 + NO_2 + M \rightarrow CCl_3CCl_2O_2NO_2 + M$$
 (4)

 $CCl_3CCl_2O_2 + HO_2 \rightarrow products$ (5)

$$CCl_3CCl_2O_2 + R'O_2 \rightarrow products$$
 (6)

The relative importance of reactions 3-6 depends on the concentration of the reactants and the rate constants. In urban areas reactions 3 and 4 are most important. In this work the rate of reaction 3 and the fate of the CCl₃CCl₂O radical were studied.

2. Experimental Section

Pulse Radiolysis Setup. The pulse radiolysis transient UV absorption spectrometer and the experimental procedure used in the present work have been described in detail before⁶⁻⁸ and will only be discussed briefly here.

 $CCl_3CCl_2O_2$ radicals were generated by the irradiation of SF₆/ CCl_3CCl_2H/O_2 gas mixtures at 296 ± 2 K in a 1 L stainless steel reaction cell with a 30 ns pulse of 2 MeV electrons from a Febetron 705B field emission accelerator. The radiolysis dose was varied by insertion of stainless steel attenuators between the accelerator and the reaction cell. SF₆ was always in great

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excess and was used to generate fluorine atoms:

$$SF_6 \xrightarrow{2 \text{ MeV e}} F + \text{ products}$$
 (7)

$$F + CCl_3CCl_2H \rightarrow CCl_3CCl_2 + HF$$
 (8)

$$CCl_3CCl_2 + O_2 + M \rightarrow CCl_3CCl_2O_2 + M$$
 (2)

Transient absorptions were followed by multipassing the output of a pulsed 150 W xenon arc lamp through the reaction cell using internal White cell optics. Total path lengths of 80 and 120 cm were used. A McPherson grating monochromator, Hamamatsu R 955 photomultiplier, and Biomation 8100 wave form digitizer were used to isolate, detect, and record the light intensity at the desired wavelength. Gas mixtures were prepared by adding one component at a time and measuring the corresponding partial pressure on a MKS Baratron-170 absolute membrane manometer with a resolution of 10^{-5} bar. Reagent concentrations used were as follows: SF₆, 989-997 mbar; CCl₃-CCl₂H, 0-3 mbar; O₂, 0-8 mbar; NO, 0.18-0.71 mbar. All experiments were performed at 296 K. Ultrahigh-purity O₂ was supplied by L'Air Liquide. SF₆ (99.9%) was supplied by Gerling and Holz. NO (>98%) was provided by Linde Technische Gase, and CCl₃CCl₂H (99.9%) was obtained from Merck. All reagents were used as received.

Prior to the present series of experiments the F atom yield at full dose was determined. This was achieved by monitoring the transient absorbance at 260 nm due to methylperoxy radicals produced by pulse radiolysis of SF₆/CH₄/O₂ mixtures as is described elsewhere.¹⁸ Using the literature value of $\sigma_{CH_3O_2}$ (260 nm) of (3.18 ± 0.32) × 10⁻¹⁸ cm² molecule^{-1,5} the F atom yield at full dose and 1000 mbar of SF₆ was determined to be (2.8 ± 0.3) × 10¹⁵ molecules cm⁻³.

FTIR–Smog Chamber System. The FTIR system was interfaced to a 140 L Pyrex reactor as described previously.⁹ Radicals were generated by the UV irradiation of mixtures of 12.9–15.2 mTorr of CCl₃CCl₂H, 0.3 Torr of Cl₂ or 0.4 Torr of F₂, and 147–700 Torr of O₂ in 700 Torr of N₂ diluent at 296 K using 22 blacklamps (760 Torr = 1013 mbar). The loss of reactants and formation of products were monitored by FTIR spectroscopy, using an analyzing path length of 27 m and a resolution of 0.25 cm⁻¹. Infrared spectra were derived from 32 coadded spectra. CCl₃CCl₂H, CCl₃C(O)Cl, and COCl₂ were monitored using their characteristic features over the wavenumber ranges 700–850, 700–1900, and 800–900 and 1700–1860 cm⁻¹, respectively. Reference spectra were acquired by expanding known volumes of reference materials into the reactor.

3. Results and Discussion

Absorption Spectrum of CCl₃CCl₂. Following the radiolysis of mixtures of 3 mbar of CCl₃CCl₂H and 997 mbar of SF₆ a rapid (complete within $5-10 \ \mu$ s) rise in the absorbance was observed followed by a slower decay. An example of an absorption transient is shown in Figure 1. A series of experiments were performed to determine the maximum radiolysis dose that can be used without loss of CCl₃CCl₂ radicals through secondary chemistry such as reactions 9 and 10:

$$CCl_3CCl_2 + CCl_3CCl_2 \rightarrow products$$
 (9)

$$F + CCl_3CCl_2 \rightarrow products$$
 (10)

The maximum absorption at 230 nm was measured as a function of radiolysis dose, and the result is plotted in Figure 2. It can be seen that the measured absorbance varies linearly with the



Figure 1. Absorption transient at 255 nm following the radiolysis of a mixture of 3 mbar of CCl_3CCl_2H and 997 mbar of SF_6 . The radiolysis dose used was 42% of full dose.



Figure 2. Maximum transient absorbance at 230 nm following the radiolysis mixtures of 3 mbar of CCl_3CCl_2H and 997 mbar of SF_6 as a function of radiolysis dose. The UV path length was 80 cm.

TABLE 1: Measured UV Absorption Cross Section

	d(CCLCCL)	$a(CC1,CC1,O_{1})$		d(CCLCCL)	a(CCLCCLO.)
λ,	$10^{-20} \mathrm{cm}^2$	$10^{-20} \mathrm{cm}^2$	λ,	10^{-20} cm^2	$10^{-20} \mathrm{cm}^2$
nm	molecule ⁻¹	molecule ⁻¹	nm	molecule ⁻¹	molecule ⁻¹
220	192	209	260	130	154
225	264		270		139
230	271	149	280	113	
235	278	136	290		93
240	240	145	300	77	85
245	211	159	320	50	61
250	173	164	400	0	18
255	130	176			

radiolysis dose up to 42% of maximum dose. At higher radiolysis doses the measured absorbance is smaller than that expected from a linear extrapolation of the low-dose data. We ascribe this to the consumption of CCl₃CCl₂ radicals and F atoms via reactions 9 and 10. The radiolysis dose used in the subsequent experiments was fixed at 42% of the full dose. The absorption cross section at 230 nm can be calculated using three pieces of information: (i) The F atom yield at 1000 mbar of SF₆ and full dose of (2.8 \pm 0.3) \times 10¹⁵ molecules cm⁻³, (ii) the UV path length of 80 cm, and (iii) the slope of the lowdose data in Figure 2 of 0.264 ± 0.022 . At 230 nm this gives an absorption cross section of (271 \pm 84) \times 10⁻²⁰ cm² molecule⁻¹. To map out the absorption spectrum, the analyzing wavelength was varied between 220 and 400 nm. The observed absorptions were scaled to that at 230 nm. The absorption cross sections obtained for the CCl₃CCl₂ radical are listed in Table 1 and plotted in Figure 3.



Figure 3. Measured absorption cross sections for CCl₃CCl₂.



Figure 4. Maximum transient absorbance following the radiolysis of $CCl_3CCl_2H/O_2/SF_6$ mixtures as a function of the ratio $[CCl_3CCl_2H]/[O_2]$ at 220 nm.

Reaction of F Atoms with CCl₃CCl₂H. Following the pulse radiolysis of CCl₃CCl₂H/O₂/SF₆ mixtures, there is a competition between reactions 8 and 11 for the available F atoms:

$$\mathbf{F} + \mathbf{CCl}_{3}\mathbf{CCl}_{2}\mathbf{H} \rightarrow \mathbf{CCl}_{3}\mathbf{CCl}_{2} + \mathbf{HF}$$
(8)

$$\mathbf{F} + \mathbf{O}_2 + \mathbf{M} \to \mathbf{FO}_2 + \mathbf{M} \tag{11}$$

In the presence of oxygen, CCl_3CCl_2 radicals are rapidly converted to $CCl_3CCl_2O_2$ radicals via reaction 2:

$$CCl_3CCl_2 + O_2 + M \rightarrow CCl_3CCl_2O_2 + M$$
 (2)

To determine the rate constant for reaction 8, a series of experiments was performed varying the CCl₃CCl₂H concentration from 0 to 3 mbar with the O_2 and SF_6 concentrations held constant at 8 and 990 mbar, respectively. At low concentrations of CCl₃CCl₂H the F atoms react mainly with O₂ so the observed absorption is mainly due to FO_2 radicals. As the concentration of CCl₃CCl₂H is increased, the fraction of the F atoms that react with CCl₃CCl₂H increases. At 220 nm CCl₃CCl₂O₂ radicals absorb less than FO₂ radicals. Hence, as the concentration ratio [CCl₃CCl₂H]/[O₂] is increased, the observed absorption decreases. The absorption maximum (which occurred within 20 μ s after the electron pulse) was monitored following the radiolysis of mixtures of 0-3 mbar of CCl₃CCl₂H, 8 mbar of O_2 , and 990 mbar of SF₆. The absorbances are plotted in Figure 4. The smooth line in Figure 4 is a three-parameter fit to the data using the following expression:

$$A_{\max} = \{A_{FO_2} + A_{CCl_3CCl_2O_2}(k_8/k_{11})[CCl_3CCl_2H]/[O_2]\}/$$

$$\{1 + (k_8/k_{11})[CCl_3CCl_2H]/[O_2]\}$$

where A_{max} is the maximum absorbance as a function of [CCl₃-CCl₂H]/[O₂]. A_{FO_2} and $A_{\text{CCl}_3\text{CCl}_2\text{O}_2}$ are the maximum absorbances expected if all F atoms are converted into FO₂ and CCl₃CCl₂O₂, respectively. It is assumed that all CCl₃CCl₂ radicals are converted into CCl₃CCl₂O₂ radicals. Three parameters (A_{FO_2} , $A_{\text{CCl}_3\text{CCl}_2\text{O}_2}$, and k_8/k_{11}) were varied simultaneously. The best fit was obtained with $k_8/k_{11} = 12.1 \pm 8.7$. Using $k_{11} = (1.9 \pm 0.3) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹,¹⁰ we arrive at $k_8 = (2.3 \pm 1.6) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. The quoted uncertainty for k_8 reflects uncertainties in both k_8/k_{11} and k_{11} . The value for k_8 measured using the pulse radiolysis system compares well with the value of $(2.0 \pm 0.5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ determined as a part of this work using the FTIR-smog chamber system as described later.

Absorption Spectrum of CCl₃CCl₂O₂. A series of experiments were performed radiolyzing mixtures of 3 mbar of CCl₃-CCl₂H, 8 mbar of O₂, and 989 mbar of SF₆ with the radiolysis dose varied by an order of magnitude and the UV monitoring wavelength fixed at 240 nm. The maximum absorbance observed is plotted as a function of the radiolysis dose in Figure 5. The maximum absorbance varies linearly with the radiolysis dose up to 42% of the maximum dose. At higher radiolysis doses the observed maximum absorbance is lower than expected from a linear extrapolation of the low-dose data. We ascribe this to unwanted radical-radical reactions such as

$$F + CCl_3CCl_2 \rightarrow products$$
 (10)

$$CCl_3CCl_2O_2 + CCl_3CCl_2 \rightarrow products$$
 (12)

$$F + CCl_3CCl_2O_2 \rightarrow products$$
(13)

To minimize the impact of these reactions, a radiolysis dose of 42% of the full dose was used in the following experiments. To map out the spectrum for the CCl₃CCl₂O₂ radical, experiments were performed with the UV monitoring wavelength varied over the range 220-400 nm. The UV path length was 80 cm. Mixtures of 3 mbar of CCl₃CCl₂H, 8 mbar of O₂, and 989 mbar of SF₆ were radiolyzed, and the maximum transient absorbance was measured. From the measured absorbances the absorption cross sections were quantified. Due to the competition between reactions 8 and 11, there is unavoidable consumption of F atoms via reaction with O_2 and hence formation of FO_2 radicals. CCl_3CCl_2H is a liquid at room temperature with a vapor pressure of 3 mbar. The cell was filled by introducing CCl₃CCl₂H into the cell until the saturated vapor pressure was reached (3 mbar). The low partial pressure of CCl₃CCl₂H limits the amount of O₂ that can be used without excessive FO₂ radical formation. However, sufficient O_2 must be present to ensure rapid conversion of CCl₃CCl₂ radicals into peroxy radicals. A compromise involving 3 mbar of CCl₃CCl₂H and 8 mbar of O₂ was employed. Using the rate constants for reactions 8 and 11 of $k_8 = (2.3 \pm 1.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } k_{11} = 1.9$ $\times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, we calculate that 18% of the F atoms were converted into FO₂. In Figure 6 the measured absorbances are plotted as a function of wavelength together with the absorbance that we calculate is attributable to the 18% yield of FO₂ radicals in the system. It can be seen from Figure 6 that, at low wavelengths, 50% of the observed absorption is caused by FO₂ radicals.

The absorption cross section at 240 nm was calculated using the F atom yield of $(2.8 \pm 0.3) \times 10^{15}$ molecules cm⁻³ at 1000



Figure 5. Maximum transient absorbance following the radiolysis of $CCl_3CCl_2H/O_2/SF_6$ mixtures as a function of the radiolysis dose at 240 nm.



Figure 6. Filled circles are the measured absorbances; the hollow triangles are the calculated absorbance attributed to an 18% yield of FO₂ radicals.



Figure 7. Absorption cross sections for $CCl_3CCl_2O_2$ measured in this work (O) and for CCl_3O_2 reported by Ellermann⁷ (line) and Russel et al.¹¹ (long dashed). Also plotted (short dashed) is the absorption spectrum for $CF_3CCl_2O_2$.⁴

mbar of SF₆, the UV path length of 80 cm, the absorption cross section for FO₂ at 240 nm of σ_{FO_2} (240 nm) = 180 × 10⁻²⁰ cm² molecule⁻¹, and the slope 0.147 ± 0.012 of the low-dose data in Figure 5. At 240 nm the absorption cross section was found to be (145 ± 21) × 10⁻²⁰ cm² molecule⁻¹. The transient absorptions corrected for FO₂ at different wavelengths were scaled to this value to determine the absorption cross sections. The results are given in Table 1 and are plotted in Figure 7. Also plotted in Figure 7 are the absorption spectra for CF₃CCl₂O₂⁴ and CCl₃O₂.^{7,11} The spectrum of CCl₃CCl₂O₂



Figure 8. Transient absorption at 400 nm following the radiolysis (42% of maximum dose) of a mixture of 0.37 mbar of NO, 3 mbar of CCl₃-CCl₂H, 8 mbar of O_2 , and 989 mbar of SF₆. The UV path length was 120 cm.



Figure 9. Pseudo-first-order rate constants as a function of NO concentration. The filled circles are the measured data points, and the hollow circles are the corrected data; see text for details.

reported here looks similar to the spectrum of CCl_3O_2 reported by Russel et al.¹¹ while it is significantly lower than the spectrum of CCl_3O_2 reported by Ellermann.⁷ The reason for this is unknown. Also plotted in Figure 7 is the literature spectrum of $CF_3CCl_2O_2$.⁴ This spectrum has a higher peak and less broad absorption spectrum than that of $CCl_3CCl_2O_2$.

Reaction of NO with CCl₃CCl₂O₂. Following the radiolysis of CCl₃CCl₂H/O₂/NO/SF₆ mixtures, an increase in absorption at 400 nm was observed. We ascribe this increasing absorption to NO_2 formation by reaction 3. An example of an absorption transient is shown in Figure 8. A series of experiments were performed where the NO concentration was varied from 0.18 to 0.71 mbar, with CCl₃CCl₂H, O₂, and SF₆ concentrations fixed at 3, 8, and 989 mbar, respectively. For each value of the NO concentration the rise in the absorption transient was fitted using a first-order exponential rise expression, and a pseudo-first-order rate constant was obtained. In all cases, the fit was started at $2-3 \ \mu s$ after the radiolysis pulse to allow sufficient time for the $CCl_3CCl_2O_2$ radicals to be formed. Figure 9 shows the measured pseudo-first-order rate constants as a function of NO concentration. Linear least-squares analysis gives $k_3 = (4.1 \pm$ 0.5) \times 10⁻¹² cm³ molecule⁻¹ s⁻¹ and an intercept of (4.0 \pm 0.6) \times 10⁴ s⁻¹. To investigate the origin of the intercept, simulations using the Chemsimul package¹² were performed. A mechanism consisting of reactions 2, 3, 4, 6, and 8 using k_2 = 3 × 10⁻¹² and $k_4 = 6 \times 10^{-12}$ assumed by analogy to other peroxy radicals⁴ $k_6 = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (assumed equal to $k_{\text{CCl}_{3}\text{O}_{2}+\text{CCl}_{3}\text{O}_{2}^{4}}$ and $k_{8} = 2.3 \times 10^{-12} \text{ cm}^{3} \text{ molecule}^{-1}$

 s^{-1} (this work). It was assumed that the CCl₃CCl₂O radical releases a Cl atom that reacts with either NO, $k_{Cl+NO} = 4 \times$ 10^{-12} , ¹³ or NO₂, $k_{Cl+NO_2} = 4 \times 10^{-11}$. ¹³ The rate constant for the decomposition of CCl₃CCl₂O was assumed to be the same as that of CCl₃O, 8×10^6 s⁻¹.¹⁴ The corrections were carried out as follows. Using the chemical mechanism above and k_3 $= 6.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a simulated transient was obtained for each data point. These transients were fitted using a first-order expression. The simulated rise in absorption followed pseudo-first-order kinetics with rate constants which were different from the expected value given by $k_3[NO]$. Corrections for the effect of unwanted reactions were computed for each data point. The corrected data are plotted as hollow circles in Figure 9. Linear least-squares analysis of the corrected data gives $k_3 = (6.2 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and an intercept of $(-0.55 \pm 1.00) \times 10^4$ s⁻¹. In view of the substantial corrections applied, we choose to add an additional 20% uncertainty to the result, giving $k_3 = (6.2 \pm 1.6) \times 10^{-12}$ cm^3 molecule⁻¹ s⁻¹.

This rate constant is of similar magnitude but somewhat lower than the rate constants found for the reactions of other halogenated ethylperoxy radicals with NO. For example, $k_{\rm RO_2+NO}$ for $\mathbf{R} = CF_3CF_2$, CHF_2CF_2 , CF_3CH_2 , CF_3CFCI , CF_3CCIH , and CCl_3CH_2 are >8.4 × 10⁻¹²,¹⁵ >9.2 × 10⁻¹²,¹⁵ (1.2 ± 0.3) × 10⁻¹¹,¹⁶ (1.5 ± 0.6) × 10⁻¹²,¹⁷ (1.0 ± 0.3) × 10⁻¹¹,¹⁸ and >6.1 × 10⁻¹² cm³ molecule⁻¹ s⁻¹,¹⁹ respectively. The reason why k_3 is lower than the average of the rate constants above could be steric hindrance by the five Cl atoms in the $CCl_3CCl_2O_2$ radical.

Relative Rate Studies of the Reactions of Cl and F Atoms with CCl₃CCl₂H. Prior to investigating the atmospheric fate of CCl₃CCl₂O radicals, relative rate experiments were performed using the FTIR system to investigate the kinetics of reactions 8 and 14. The techniques used are described in detail elsewhere.²⁰ Photolysis of molecular halogen was used as a source of halogen atoms.

$$Cl_{2} (F_{2}) + h\nu \rightarrow 2Cl + (2F)$$
$$+ CCl_{3}CCl_{2}H \rightarrow CCl_{3}CCl_{2} + HCl \qquad (14)$$

$$F + CCl_3CCl_2H \rightarrow CCl_3CCl_2 + HF$$
(8)

The kinetics of reaction 14 were measured relative to reactions 15 and 16, while reaction 8 was measured relative to reaction 17.

Cl

$$Cl + CD_3H \rightarrow products$$
 (15)

$$Cl + CH_4 \rightarrow CH_3 + HCl$$
 (16)

$$\mathbf{F} + \mathbf{CH}_2 \mathbf{F}_2 \rightarrow \mathbf{CHF}_2 + \mathbf{HF} \tag{17}$$

The observed losses of CCl₃CCl₂H versus that of CD₃H and CH₄ in the presence of Cl atoms and CCl₃CCl₂H versus CH₂F₂ in the presence of F atoms are shown in Figures 10 and 11. As shown in Figure 10, there was no discernible difference between data obtained in 700 Torr of either diluent N₂ or diluent air. In the study of the reaction of F atoms with CCl₃CCl₂H care must be taken to avoid, or correct for, complications caused by the generation of Cl atoms following reaction 8. Cl atoms react with CCl₃CCl₂H a factor of $(5.2 \times 10^{-14}/3.2 \times 10^{-14}) = 1.6$ times faster than with CH₂F₂.²¹ To minimize complications caused by Cl atoms, the initial concentration of CCl₃CCl₂H was kept as low as practicable. The initial concentration ratio [CCl₃CCl₂H]/[CH₂F₂] was varied over the range 0.15–0.25 with



Figure 10. Plot of the decay of CCl_3CCl_2H versus those of CH_4 and CD_3H in 700 Torr of air (filled symbols) or nitrogen (open symbols) at 296 K in the presence of Cl atoms.



Figure 11. Plot of the decay of CCl_3CCl_2H versus that of CH_2F_2 in 700 Torr of air at 296 K in the presence of F atoms.

no observable effect on the measured value of k_8/k_{17} . It seems reasonable to conclude that our measurement of k_{8}/k_{17} is free from major complications associated with Cl atoms. Linear least-squares analysis of the data in Figures 10 and 11 gives $k_{14}/k_{15} = 2.32 \pm 0.16, k_{14}/k_{16} = 0.51 \pm 0.03$, and $k_8/k_{17} = 0.59$ \pm 0.07. To investigate the effect that Cl atoms could have on k_8/k_{17} , the chemistry in the chamber was modeled. The chemical mechanism used assumed that the loss of each molecule of CCl₃CCl₂H gave one Cl atom, that Cl atoms react with either CCl₃CCl₂H or CH₂F₂, and that CCl₃CCl₂H is 1.6 times more reactive toward Cl atoms than CH_2F_2 . With $[CCl_3CCl_2H]_0/$ $[CH_2F_2] = 0.2$, k_8/k_{17} is predicted to be overestimated by 20%. We choose to quote a final value of $k_8/k_{17} = 0.47 \pm 0.07$. Using $k_{15} = 2.3 \times 10^{-14}, 20 \ k_{16} = 1.0 \times 10^{-13}, 21 \ \text{and} \ k_{17} = 4.3 \times 10^{-12}, 21 \ \text{gives} \ k_{14} = (5.3 \pm 0.2) \times 10^{-14}, \ k_{14} = (5.1 \pm 0.3) \times 10^{-14}, \ k_{15} = (5.1 \pm 0.3) \times 10^{-14}, \ k_{16} =$ 10^{-14} , and $k_8 = (2.0 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. We estimate that potential systematic errors associated with uncertainties in the reference rate constants could add additional 10% and 20% ranges to the uncertainties for k_{14} and k_8 , respectively. Propagating this additional uncertainty gives values of $k_{14} = (5.3 \pm 0.6) \times 10^{-14}$, $k_{14} = (5.1 \pm 0.6) \times 10^{-14}$ 10^{-14} , and $k_8 = (2.0 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We choose to cite a final value of k_{14} , which is an average of those determined using the two different reference compounds together with error limits which encompass the extremes of the two individual determinations. Hence, $k_{14} = (5.2 \pm 0.7) \times 10^{-14}$ cm^3 molecule⁻¹ s⁻¹. The quoted error reflects the accuracy of the measurements.

The value of k_8 determined using the FTIR technique is in good agreement with the determination of $k_8 = (2.3 \pm 1.6) \times$

TABLE 2: Product Yields^a following the Irradiation of CCl₃CCl₂H/(Cl₂ or F₂)/O₂ Mixtures in 700 Torr of N₂ Diluent

expt	$[CCl_3CCl_2H]_0$	$[X_2]_0{}^b$	[O ₂] ^b	$t_{\rm UV}~({\rm min})^c$	Δ [CCl ₃ CCl ₂ H]	[CCl ₃ COCl]	Δ [COCl ₂]
1	12.9	0.3 (Cl ₂)	147	0.5	5.03	4.44	1.73
				1.0	8.77	7.55	2.86
				1.5	11.1	9.59	3.80
2	13.9	0.3 (Cl ₂)	700	0.5	5.00	4.39	1.60
				0.75	6.81	5.77	2.13
				1.25	9.59	8.26	3.13
3	15.2	$0.4 (F_2)$	147	2	1.90	1.69	0.53
				7	6.08	5.19	1.73
				12	8.51	7.28	2.46

^a Concentrations in units of mTorr. ^b Units of Torr. ^c UV lamps were not equipped with preignition coils; hence the exact irradiation times may vary.

 10^{-12} cm³ molecule⁻¹ s⁻¹ using the pulse radiolysis technique in the present work. There are no literature data for k_8 with which to compare our results. While there have been no previous studies of k_{14} at ambient temperature, Goldfinger et al.²² used a relative rate technique at 385–480 K to derive k_{14} = $1.05 \times 10^{-11} \exp(-1660/T)$, which at 296 K gives $k_{14} = 4 \times 10^{-14} \text{ cm}^3$ molecule⁻¹ s⁻¹, consistent with the results from the present work.

Study of the Atmospheric Fate of CCl₃CCl₂O Radicals. To determine the atmospheric fate of the alkoxy radical CCl₃-CCl₂O, three experiments were performed in which CCl₃CCl₂H/ O_2/Cl_2 and CCl₃CCl₂H/ O_2/F_2 mixtures at a total pressure of 700 Torr made up with N₂ diluent were irradiated in the FTIR-smog chamber system. The experimental conditions and results are given in Table 2. The loss of CCl₃CCl₂H and the formation of products were monitored by FTIR spectroscopy. CCl₃CCl₂O radicals formed in the chamber in reaction 18 will either eliminate a Cl atom to give CCl₃C(O)Cl or undergo C-C bond scission to give COCl₂ and CCl₃ radicals.

$$CCl_3CCl_2O_2 + CCl_3CCl_2O_2 \rightarrow 2CCl_3CCl_2O + O_2$$
 (18)

$$CCl_3CCl_2O + M \rightarrow CCl_3C(O)Cl + Cl + M$$
 (19)

$$CCl_3CCl_2O + M \rightarrow CCl_3 + COCl_2 + M$$
 (20)

 CCl_3 radicals formed in reaction 20 will be converted into $COCl_2$ via addition of O_2 ; reaction with peroxy radicals ($CCl_3CCl_2O_2$ or CCl_3O_2) will give CCl_3O radicals, which will then loose a Cl atom to give $COCl_2$.⁷

Two products were observed following the oxidation of CCl_3CCl_2H ; $CCl_3C(O)Cl$ and $COCl_2$. Figure 12 shows the results obtained in this work. As seen in Figure 12, the formation of CCl₃C(O)Cl and COCl₂ were linear functions of the CCl₃CCl₂H loss. There was no discernible effect of O_2 partial pressure or the degree of CCl₃CCl₂H consumption. Results obtained using Cl and F atom initiation were indistinguishable, suggesting the absence of systematic errors caused by unwanted radical-radical reactions involving Cl or F atoms. To provide information on the behavior of CCl₃C(O)Cl and $COCl_2$ in the chamber, mixtures of $CCl_3C(O)Cl$ and $COCl_2$ in air with, and without, added Cl₂ were prepared, allowed to stand in the dark for 5 min, and then irradiated for 5 min. No loss (<1%) of CCl₃C(O)Cl or COCl₂ was discernible, suggesting that under the present experimental conditions. $CCl_3C(O)Cl$ and COCl₂ are not lost by heterogeneous processes, photolysis, or reaction with Cl atoms. The absence of any discernible difference between the results of experiments using Cl and F atom initiation suggests that, under the present experimental conditions, neither $CCl_3C(O)Cl$ nor $COCl_2$ reacts to any appreciable degree with F atoms. Linear least-squares analysis of the data in Figure 12 provides molar yields for CCl₃C(O)Cl



Figure 12. Formation of $CCl_3C(O)Cl$ and $COCl_2$ as functions of the loss of CCl_3CCl_2H following the irradiation of $CCl_3CCl_2H/(Cl \text{ or } F_2)/O_2$ mixtures. Open circles are results from experiments using Cl atom initiation in 700 Torr of air, filled circles were obtained using Cl initiation in 700 Torr of O₂, and diamonds represent F atom initiation in 700 Torr of air.

and COCl₂ of $86 \pm 9\%$ and $33 \pm 3\%$. Together, these two products account for $102 \pm 10\%$ of the observed loss of CCl₃-CCl₂H.

The results from the present work show that at 700 Torr total pressure and 296 K, decomposition of CCl₃CCl₂O radicals proceeds via two competing pathways: Cl atom elimination (reaction 19) and C-C bond scission (via reaction 20). If we normalize the total product yield from 102% to 100%, then it can be concluded that reaction 19 accounts for $85 \pm 9\%$ of the CCl₃CCl₂O radicals while reaction 20 accounts for $15 \pm 2\%$.

The Cl atom initiated gas-phase oxidation of CCl₃CCl₂H has been studied previously by Huybrechts et al.²³ at 353 and 373 K. Huybrechts et al.²³ report that $85 \pm 5\%$ of CCl₃CCl₂H is converted into CCl₃C(O)Cl with the remaining $15 \pm 5\%$ appearing as COCl₂. No dependence on temperature was reported. Also, no effect of added third bodies was observed (up to 286 Torr of N₂ or 55 Torr of CCl₃C(O)Cl was added to reaction mixtures containing initially 200 Torr of Cl2 and 40-60 Torr of CCl₃CCl₂H).²³ The results of Huybrechts et al.²³ are indistinguishable from those measured in the present work at 296 K, showing that the relative importance of reactions 19 and 20 as loss mechanisms for CCl₃CCl₂O radicals is unchanged over the temperature range 296-373 K. From this observation it can be concluded that there is no more than $0.5 \text{ kcal mol}^{-1}$ difference in the activation energies for reactions 19 and 20. This conclusion together with the expectation that reactions 19 and 20 are at, or near, the high-pressure limit under atmospheric conditions (supported by the absence of any discernible effect of added third bodies noted above) means that the fate of CCl₃CCl₂O radicals determined in the present work is appropriate for essentially all regions of the atmosphere. Hence, we conclude that in the atmosphere 85% of CCl₃CCl₂O radicals will eliminate a Cl atom and 15% will undergo C-C bond scission.

The behavior of CCl₃CCl₂O radicals can be compared with those of the two structurally similar alkoxy radicals, CF₃CCl₂O and CF₃CF₂O, formed during the atmospheric degradation of HCFC-123 and HFC-125, respectively. In the atmosphere CF₃CCl₂O radicals undergo Cl atom elimination to give CF₃C(O)Cl exclusively,²⁴⁻²⁶ whereas CF₃CF₂O radicals undergo C-C bond scission exclusively.^{25,27,28} In view of the strength of the C-F bond, it is not surprising that CF₃CF₂O radicals undergo C-C bond scission in preference to α -halogen atom elimination. The increased importance of C-C bond scission in CCl₃CCl₂O radicals compared with CF₃CCl₂O radicals implies either a strengthened C-Cl bond, or weakened C-C bond, or both, in CCl₃CCl₂O compared to CF₃CCl₂O.

It is worthwhile to note that experiment 3 (see Table 2) sheds some light on the mechanism of F atom attack on CCl₃CCl₂H. Throughout this work it has been assumed that reaction 8 proceeds via H atom abstraction to give CCl_3CCl_2 radicals. Another possibility is Cl atom abstraction. As shown in Figure 12, the product yields following F atom initiated oxidation were indistinguishable from those following Cl atom initiation, suggesting that the reaction of F atoms with CCl_3CCl_2H proceeds predominately via H atom abstraction.

4. Atmospheric Implications

Following release into the atmosphere, CCl₃CCl₂H will react with OH radicals. Kinetic data for the reaction of OH radicals with CCl₃CCl₂H are limited to 292 K, where $k(OH+CCl_3 CCl_2H$ = 2.3 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹.³ This rate constant is $(2.3 \times 10^{-13}/8.7 \times 10^{-15}) = 26$ times greater than that of methylchloroform, which is known to be removed from the atmosphere solely by reaction with OH radicals with an atmospheric lifetime of 5.7 years.²⁹ Hence, the atmospheric lifetime of CCl₃CCl₂H with respect to OH radical attack is approximately 2.5 months. To quantify the potential importance of photolysis as an atmospheric loss mechanism for CCl₃CCl₂H, we measured its UV absorption spectrum. There was no measurable absorption ($\sigma < 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$) at wavelengths longer than 245 nm. Absorption by ozone in the stratosphere prevents radiation with wavelengths shorter than 290 nm from reaching the troposphere (see Figure 2 in ref 30). Photolysis is not a significant loss mechanism for CCl₃CCl₂H. The atmospheric lifetime of CCl₃CCl₂H is dictated by reaction with OH radicals only. Reaction with OH gives CCl₃CCl₂ radicals which are rapidly (within 1 μ s) converted into $CCl_3CCl_2O_2$ radicals.

We have shown here that CCl₃CCl₂O₂ radicals react with NO to produce NO₂ and (by inference) CCl₃CCl₂O radicals. using $k_3 = (7.0 \pm 2.3) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ together with an estimated background tropospheric NO concentration of 2.5 × 10⁸ cm⁻³,³¹ the lifetime of CCl₃CCl₂O₂ radicals with respect to reaction 3 is calculated to be 9.5 min. Reaction 3 is likely to be an important atmospheric loss of CCl₃CCl₂O₂ radicals. We have shown here that two decomposition reactions are important loss mechanisms for CCl₃CCl₂O radicals. Elimination of a Cl atom accounts for 85% of CCl₃CCl₂O radicals with C-C bond scission accounting for the remaining 15%. The carbonyl products formed (CCl₃C(O)Cl and COCl₂) will be photolyzed and/or incorporated into rain-cloud-sea water within a period of $20-60 \text{ days}^{32}$ and will not be effective in transporting Cl to the stratosphere.

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