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Flash Photolysis-Time-Resolved UV Spectroscopy of the CF₃CFHO₂ Self-Reaction

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The self-reaction of CF₃CFHO₂ has been studied via time-resolved ultraviolet spectroscopy over the temperature range 211-372 K. The absorption spectrum of CF₃CFHO₂ extends from 190 to 275 nm with a maximum cross section of $(5.2 \pm 0.3) \times$ 10⁻¹⁸ cm² molecule⁻¹ at 213 nm. The UV absorbance of the reaction mixture decreases and shifts to the blue as the reaction progresses. This is consistent with the CF₃CFHO₂ self-reaction producing CF₃CFHO, the alkoxy radical then decomposing to yield CF₃, which adds molecular oxygen to form CF₃O₂. The CF₃CFHO₂ self-reaction has a negative temperature dependence with rate constant given by $k_1 = (7.8 \pm 1.3) \times 10^{-13} e^{(605 \pm 40)/T}$ cm³ s⁻¹. The rate of alkoxy radical dissociation, at 230 Torr of total pressure, is $k_{2a} = (3.7 \pm 0.7) \times 10^7 e^{-(2200 \pm 150)/T} s^{-1}$. The rate constants for CF₃O₂ reaction with CF₃CFHO₂ and itself are determined to be $k_8 = (8 \pm 3) \times 10^{-12}$ and $k_9 = (1.8 \pm 0.5) \times 10^{-12}$ cm³ s⁻¹, respectively, at 297 K.

I. Introduction

Over the past few years, an increasing wealth of data has been collected supporting the postulate that chlorofluorocarbon (CFC) compounds are transported into the stratosphere where they are photolyzed to produce atomic chlorine and thereby contribute to the catalytic destruction of stratospheric ozone.¹ The environmental ramifications of this have led to international agreements to phase out and eventually eliminate the manufacture and use of these compounds.² The principal strategy in finding CFC replacements has been to examine chlorine- and fluorine-substituted methane, ethane, and propane species which retain at least one hydrogen atom, namely, the hydrochlorofluorocarbon (HCFC) compounds. The reason for this strategy is that, while retaining many of the useful physical properties of the CFC's, the HCFC compounds, by virtue of their hydrogen atoms, are significantly more reactive than CFC's toward OH radicals and are removed before they reach the stratosphere.³ However, comparatively little is currently known about the tropospheric chemistry of the HCFC molecules. The very reactivity which makes these compounds safe

HFC-134a (CF_3CFH_2) is the designated replacement for CFC-12 as an automobile refrigerant. Because it is unreactive with oxidizers such as oxygen and ozone and because its has very small UV absorption cross sections at wavelengths penetrating into the troposphere,⁴ the principal removal mechanism of HFC-134a is expected to be via

$$CF_3CFH_2 + OH \rightarrow CF_3CFH + H_2O$$

Recent measurements of the UV absorption spectrum of CF3CFH2 and its reaction rate constant with OH indicate that HFC-134a has an expected tropospheric lifetime of approximately 17 years.^{3,4} The hydrofluorocarbon radical produced by the above hydrogen-abstraction reaction will, in the presence of >10 Torr of O_2 and 50 Torr of total pressure, add molecular oxygen on a microsecond time scale⁵

$$CF_3CFH + O_2 + M \rightarrow CF_3CFHO_2 + M$$

to form the corresponding peroxy radical.

Peroxy radicals are relatively stable in the troposphere. They are unreactive toward the major components of the atmosphere

with respect to the stratosphere may potentially pose environmental problems in the troposphere.

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and are primarily removed by reaction with NO, NO₂, and other peroxy radicals. Wallington and Nielsen⁶ found a large rate constant for reaction of CF_3CFHO_2 with NO and discussed the atmospheric implications thereof. They also measured absolute UV absorption cross sections for the CF_3CFHO_2 radical and found them to be approximately 50% larger than the previous values reported by Jemi-Alade et al.⁷

The present paper examines the kinetics of the CF_3CFHO_2 self-reaction by monitoring the change in UV absorbance of the reaction mixture with time. The study of this reaction is made both more difficult and more interesting by the fact that the UV spectrum not only diminishes with time but also shifts to the blue. A recent FTIR product study⁸ revealed two channels for the self-reaction

$$CF_3CFHO_2 + CF_3CFHO_2 \rightarrow 2CF_3CFHO + O_2$$
 (1a)

$$CF_3CFHO_2 + CF_3CFHO_2 \rightarrow CF_3COF + CF_3CFHOH + O_2$$
 (1b)

with 84% of the reaction proceeding via channel 1a. The alkoxide produced in reaction 1a either decomposes or reacts with oxygen

$$CF_3CFHO \rightarrow CF_3 + HC(O)F$$
 (2a)

$$CF_3CFHO + O_2 \rightarrow CF_3COF + HO_2$$
 (2b)

with channel 2b dominating for O_2 pressures greater than an atmosphere. Under the experimental conditions of the present study, channel 2a predominates and leads to the formation of CF_3O_2 via

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$$
 (3)

By fitting the time-resolved UV spectra of the reaction mixture between 190 and 300 nm to reference spectra of CF_3CFHO_2 and CF_3O_2 , we are able to determine the changes in the concentrations of these species over time. When compared against predictions of a kinetic model, these concentration profiles provide us with measures for the CF_3CFHO_2 and CF_3O_2 self-reactions and the $CF_3CFHO_2 + CF_3O_2$ cross reaction rate constants and the CF_3CFHO decomposition lifetime.

In order to appreciate the atmospheric implications of CF_3CFH_2 photooxidation, one needs to understand the temperature dependence of the reactions involved. Previous work⁸ examined the effect of temperature on the relative rates of reactions 2a and 2b. Here we report direct measurements of the temperature-dependent rate constants for reactions 1 and 2a.

The following section describes the time-resolved UV spectrometer used in these experiments. Section III presents the UV spectrum of CF_3CFHO_2 , the absolute intensity of which supports the cross sections previously reported by Wallington and Nielsen.⁶ A discussion of the self-reaction mechanism and our kinetic measurements are given in section IV.

II. Experimental Section

The flash photolysis-time-resolved UV spectrometer⁹ used for the kinetics studies is shown in Figure 1. A mixture of CF₃CFH₂, N₂, O₂, and 5% F₂/He is flowed through a quartz-jacketed, foam-insulated, reaction cell measuring 3.2-cm in diameter by 51 cm in length. Light (351 nm) from an excimer laser (Lambda Physik LPX-300) passes longitudinally through the cell, exciting F₂ into the repulsive A¹II_u state and thereby producing F atoms. This state obtains a maximum cross-sectional value of approximately 2.3×10^{-20} cm² at 290 nm; at 351 nm, the absorption cross section is roughly 4×10^{-21} cm².¹⁰ Under the typical concentrations of 8×10^{16} cm⁻³ of F₂ flowing through the reaction vessel, 2×10^{14} cm⁻³ F atoms are produced with a 300-mJ laser pulse. The fluorine atoms rapidly produce CF₃CFHO₂ radicals via the reaction sequence

$$F + CF_3CFH_2 \rightarrow CF_3CFH + HF$$
 (4)

$$CF_3CFH + O_2 + M \rightarrow CF_3CFHO_2 + M$$
 (5)

CF₃CFH₂ and O₂ concentrations were adjusted so that the half-life for CF₃CFHO₂ formation was less than 10 μ s.



Figure 1. Schematic diagram of the flash photolysis-time-resolved UV spectrometer.

Broad-band UV light from a deuterium lamp counterpropagates the cell and is focused onto the slits of an Instruments SA HR320 0.32 meter monochromator. The use of dichroic beam-steering mirrors for the excimer radiation allows the transmission of radiation from 180 to 330 nm. The dispersed light is detected by a gated, intensified, diode array (Princeton Instruments IPDA-700SB detector and ST1000 controller) at a specified time delay (1 μ s to 100 ms) from the photolysis laser pulse. Wavelength calibration is obtained by comparison to the spectrum of a lowpressure mercury lamp. The instrument resolution is 2–3 nm. A mechanical shutter is employed to prevent the cw probe beam from impinging on the detector between photolysis pulses in order to overcome a small amount of light leakage through the gate which occurs at UV wavelengths.

Absorption spectra are obtained using Beer's law, with I_0 collected 40 ms prior to each photolysis pulse and I measured at a preset delay time following photolysis. Typically 750 such data pairs were averaged for each spectrum. This procedure eliminates contributions to the spectrum from UV absorption by reactant molecules or long-lived products and reduces systematic variations in reaction conditions such as lamp intensity, gas flow rates, etc., that would be incurred by separate measurements of I and I_0 . The resultant spectrum thus reflects the difference in concentration of absorbing species before and after the photolysis pulse.

Temperature control is achieved by flowing an ethylene glycol/water mixture or methanol refrigerant through the reaction cell jacket. The refrigerant temperature is maintained by a Neslab ULT-80dd recirculating controller which can be set between 90 and -60 °C. The reactant gases, except for the hydrocarbon (CF₃CFH₂ or C₂H₆), were precooled by passing them through two stainless steel chambers at the refrigerant temperature prior to their introduction into the reaction cell. The hydrocarbon was added directly to the cell in order to avoid dark reaction with F₂. The gas temperature was measured by inserting a thermocouple approximately midway into the cell while flowing the gases under conditions identical to those used for measuring the UV spectra. Even at the extreme ends of the range, the precooling ensured a gas temperature within 10 °C of the setpoint.

Regulation of the gas flows was accomplished with Tylan FC260 flow controllers, with the exception of the 5% F_2/He mixture, the flow rate of which was adjusted by a needle valve. The composition of the reactant gas mixture was ascertained by timing the pressure rise of each gas when flowing into a constant volume and multiplying the corresponding fractional flow rate by the total pressure. The total reactant gas pressure was measured by Baratron capacitance manometers at the entrance and exit of the reaction vessel. A typical reaction mixture consisted of 15 Torr of CF₃CFH₂, 5 Torr of O₂, 60 Torr of 5% F_2/He , and 150 Torr of N₂.

III. UV Absorption Spectra

A. CF₃CFHO₂. In order to determine accurately the absolute absorption intensities for transitory species such as CF₃CFHO₂,

ΤA	BL	E	I:	UV	Absor	ntion	Cross	Section
-		_	**	•••			0.000	

wavelength,	$\sigma(CF_3CFHO_2),$	$\sigma(CF_3O_2),^a$	$\sigma(CF_3CFHO),$
nm	10^{-18} cm^2	10^{-18} cm^2	10^{-18} cm^2
307.8	0.05	0.15	
302.7	0.08	0.09	
297.5	0.07	0.02	
292.4	0.17	0.03	0.24
287.2	0.17	0.05	0.35
282.1	0.22	0.13	0.39
276.9	0.36	0.10	0.51
271.8	0.53	0.12	0.77
266.7	0.70	0.16	0.90
261.5	0.97	0.21	0.97
256.4	1.32	0.33	0.84
251.2	1.79	0.51	0.58
246.1	2.40	0.80	0.28
240.9	2.92	1.21	0.14
235.8	3.58	1.77	
230.7	4.19	2.43	
225.5	4.69	3.11	
220.4	5.01	3.72	
215.2	5.16	4.14	
210.1	5.04	4.30	
205.0	4.62	4.15	
199.8	3.92	3.74	
194.7	3.22	3.18	
189.5	2.76	2.71	

^aReference 11.

one ideally prefers conditions under which the radical is rapidly formed but only slowly removed. Rapid formation of CF_3CFHO_2 can be ensured by using a reaction mixture containing high concentrations of CF_3CFH_2 and O_2 . There is, however, one caveat. If there is too much O_2 , it will compete with CF_3CFH_2 for reaction with F atoms, forming FO₂ via

$$F + O_2 + M \rightarrow FO_2 + M \tag{6}$$

The production of FO₂ interferes with the absorption cross-section measurement in two ways: First, it reduces the yield of CF₃C-FHO₂, and second, FO₂ has a UV absorption maximum at 206 nm which is 3 times more intense than the absorption maximum for CF₃CFHO₂ at 213 nm.¹¹ Fortunately, there are two ways to reduce the termolecular FO₂ formation: by reducing either the amount of O₂ or the total pressure of the reaction mixture.

Spectra of CF₃CFHO₂ were measured with the $[CF_3CFH_2]/[O_2]$ ratio ranging from 1.2 to 30 and with a total pressure between 100 and 600 Torr. Interference from FO₂ became noticeable at $[CF_3CFH_2]/[O_2] = 1.5$ and $P_{tot} = 600$ Torr. This is consistent with predictions of a 4% yield of FO₂ (implying a 12% effect on the UV spectrum of CF₃CFHO₂) under these conditions, based on the recently measured rate constants of 1.5 $\times 10^{-12}$ cm³ s⁻¹ for reaction 4,¹² 2.1 $\times 10^{-12}$ cm³ s⁻¹ for reaction 5,⁵ and 9.2 $\times 10^{-14}$ cm³ s⁻¹ for reaction 6¹² at 700 Torr of total pressure. In general, a ratio of $[CF_3CFH_2]/[O_2] = 3$ and $P_{tot} = 230$ Torr were maintained for both the UV cross-section measurements and for the time-resolved spectra reported in section IV. Under these conditions, $[FO_2] < 1\%$.

The UV absorption spectrum of CF₃CFHO₂ is shown in Figure 2, and the absorption cross sections are listed in Table I. Absolute cross sections were determined by comparing the absorbance of CF₃CFHO₂ to the absorbance of C₂H₅O₂ generated under identical conditions, except that ethane was substituted for CF₃CFH₂ in the reaction mixture. Ethyl peroxy radicals provide a convenient means of calibrating the absorption intensity because they are rapidly generated using modest ethane and oxygen concentrations and they react only very slowly with each other ($k = 5.9 \times 10^{-14}$ cm³ s⁻¹).¹³ Therefore, using the previously reported UV cross sections for the ethyl peroxy radical,⁹ it is possible to ascertain the concentration of $C_2H_5O_2$ and, thereby, the initial fluorine atom concentration. The recently reported ethyl peroxy cross sections of ref 9 represent an improvement over previous values both from the point of view that the entire spectrum is measured in a single experiment and from the calibration procedure that was employed. The cross sections are about 7% larger than the previously rec-



Figure 2. UV absorption spectrum of CF_3CFHO_2 . A spectrum of $C_2H_5O_2$, which was used to ascertain absolute absorption intensities for CF_3CFHO_2 , is provided for comparison.



Figure 3. UV absorption spectrum of CF₃CFHO.

ommended values¹⁴ but are within the latter's error bars. A recent remeasurement¹⁵ of the $C_2H_5O_2$ UV cross section reproduces these slightly larger values.

Whereas experimental conditions could be adjusted to produce rapidly the CF₃CFHO₂ radicals, their disappearance is dominated by their self-reaction. Using the self-reaction rate constant for CF₃CFHO₂ (section IV), a 5% (10%) correction to the raw absorption cross sections was required to account for the radicals lost in the 20- μ s (40- μ s) intervening between the photolysis pulse and the recording of the CF₃CFHO₂ spectrum. This correction has been applied to the CF₃CFHO₂ spectrum reported in Figure 2 and Table I.

The UV spectrum of CF_3CFHO_2 shows a symmetric, featureless, absorption band centered at 213 nm with a FWHM of approximately 50 nm. The shape and intensity are essentially similar to that of the ethyl peroxy radical (also shown in Figure 2); however, the band is shifted 28 nm to the blue. The spectrum reported here is in quantitative agreement with the absorption cross sections measured between 220 and 300 nm by Wallington and Nielsen.⁶ In contrast, the absorption maximum is 35% higher than the value given by Jemi-Alade et al.⁷ This discrepancy could be explained by the latter author's use of chlorine atoms to generate CF_3CFHO_2 radicals. Because of the very slow reaction between Cl and CF_3CFH_2 , this choice leaves the possibility that a significant fraction of the chlorine atoms react with trace impurities in the CF_3CFH_2 , producing less than the expected amount of CF_3CFHO_2 and, thereby, a smaller absorption.

B. CF₃CFHO. Time-resolved spectra of the CF₃CFHO₂ reaction mixture show the absorption intensity to decrease and shift to the blue with time, an effect due to the formation of CF₃O₂. At low temperatures, below 238 K, an additional feature becomes apparent; the time-resolved spectra show an increase and subsequent decrease of the absorption intensity in the range of 260–280 nm (see Figure 5 below). We tentatively assign this absorption feature of CF₃CFHO and display the spectrum in Figure 3. The scale for absorption intensity was arrived at by estimating the



Figure 4. Time-resolved UV spectra of the CF₃CFHO₂ reaction showing the decrease in intensity and concomitant blue shift of the absorption spectrum as a function of time. The spectra are taken at 297 K. The dashed lines are best fits of the absorbance to the CF₃CFHO₂ and CF₃O₂ reference spectra, respectively.

number density of alkoxy radicals from the loss of CF_3CFHO_2 radicals at early times, assuming that the yield of reaction 1a is 84%. The alkoxy radical is generated as a product of the CF_3 - $CFHO_2$ self-reaction. At higher temperatures, its decomposition to CF_3 is rapid; however, as the reaction mixture is cooled, the alkoxy radical develops a sufficiently long lifetime to be observed. A more detailed account of the reasoning for this assignment is made in section IV.

IV. Kinetics

A. Time-Resolved Spectra. The time-resolved UV spectra of the CF₃CFHO₂ reaction mixture reveal the temporal changes in the concentrations of the UV absorbing species. Figure 4 illustrates this point. The principal effect of time is an overall decrease in absorbance, evidence that peroxy radicals are being lost by reaction. However, the absorbance also shifts toward shorter wavelength. The fit of the time-resolved spectra to the reference spectrum of CF₃CFHO₂ is very good at t = 0.01 ms but becomes progressively worse at longer times. This effect is indicative of a second UV absorbing species which appears as a consequence of the CF₃CFHO₂ self-reaction and is then itself consumed by reaction.

An appropriate candidate for the second species is CF_3O_2 . The FTIR studies of Wallington et al.⁸ indicate that self-reaction of CF_3CFHO_2 radicals proceeds via two pathways, reactions 1a and 1b, with a branching probability of 0.84 and 0.16, respectively. Under conditions of low O_2 partial pressure, such as in the present experiments, the major product, CF_3CFHO , decomposes via reaction 2a to yield CF_3 radicals. In the presence of O_2 , which is necessary to generate CF_3CFHO_2 in the first place, these rapidly add O_2 to form CF_3O_2 radicals. Furthermore, CF_3O_2 absorbs¹¹ at 210 nm with an intensity comparable to that of CF_3CFHO_2 . Consistent with this, the time-resolved spectra are increasingly better fit at long times by the CF_3O_2 reference spectrum as opposed to that of CF_3CFHO_2 . This is demonstrated by the dashed curve corresponding to t = 2.0 ms in Figure 4.

Of the other two CF₃CFHO₂ self-reaction products, CF₃COF is easily eliminated. It has a UV absorption band¹² with $\lambda_{max} =$ 188 nm and a cross section of 2.8 × 10⁻²⁰ cm² at λ_{max} . This species has the wrong wavelength dependence and is too weak an absorber to account for the blue shift in the time-resolved spectra of the CF₃CFHO₂ self-reaction, particularly as it only appears in 16% yield. It is also unlikely that CF₃CFHOH, a closed-shell species without π bonds, would absorb sufficiently at ca. 210 nm to account for the second absorbing species.

Two other UV absorbing species that might account for the changes in the UV spectrum with time are FO_2 and HO_2 . Both of these have absorption spectra^{11,14} which peak in the vicinity of 210 nm. As discussed in section IIIA, FO_2 arises from a competition between F atom reaction with CF_3CFH_2 and O_2 and should be sensitive to O_2 partial pressure and total pressure. The



Figure 5. Time-resolved UV spectra of the CF_3CFHO_2 reaction at 216 K showing the initial increase and subsequent decrease in absorption intensity in the region of 260–280 nm. This absorption is tentatively assigned to CF_3CFHO .

observed blue shift in the time-resolved spectra is sensitive to neither so long as the $[CF_3CFH_2]/[O_2]$ ratio and P_{tot} have been set to values limiting $[FO_2]/[CF_3CFHO_2]$ to less than about 0.02. While HO₂ cannot be eliminated on spectroscopic grounds, we can estimate $[HO_2]$ from the relative rate data of Wallington et al.;⁸ that is, $k_{2a}/k_{2b} = 1.4 \times 10^{19}$ cm⁻³ at 230 Torr and $[CF_3O_2]/[HO_2] = 86$ at 5 Torr of O₂. Therefore, neither FO₂ nor HO₂ can account for the observed spectral shift because of their very low expected concentrations.

The changes in the time-resolved spectra become somewhat more complex at temperatures below 238 K owing to the appearance of a feature which must be assigned to a third UVabsorbing species. In an expanded view of the UV spectrum, Figure 5 shows the increase and subsequent decrease in absorption intensity between 260 and 280 nm. The appearance of the new feature is inversely correlated with the decrease in CF₃CFHO₂ concentration at early times, indicating that it is a primary product of the self-reaction. It appears before CF₃O₂ can be detected and then disappears before the CF_3O_2 does, suggesting that it is a precursor of the latter radical. This observation, coupled with the expectation that the decomposition of CF₃CFHO decreases with decreasing temperature, suggests that CF₃CFHO is the new species. No previous reports of the UV spectrum of this alkoxy radical exist; thus, a direct identification is not possible. It is, however, possible to compare its UV spectrum with those of other alkoxy radicals. The laser-induced fluorescence spectrum¹⁶ of the $A \leftarrow X$ band of CF₃O has been observed between 300 and 400 nm, whereas the corresponding transition¹⁷ for CH₃O lies in the 270-420-nm wavelength region. At 260-280 nm, the present absorption feature lies at wavelengths somewhat shorter, but not inconsistent, with those expected of alkoxy radicals.

Even though one might expect $[HO_2]/[CF_3O_2]$ and $[FO_2]/[CF_3O_2]$ to increase as the temperature is lowered, the possibility that the third spectral feature is a consequence of HO₂ or FO₂ can be dismissed on spectral grounds. While the yield of CF₃C-FHO and CF₃CFHOH could also increase as the temperature is lowered, they can likewise be eliminated because their UV spectra do not match that of the new feature.

On the basis of the above observations, we arrive at the reaction mechanism summarized in Table II to describe the chemistry originating from the CF_3CFHO_2 radical. Besides reactions 1–3, introduced above, it incorporates the reactions

$$CF_3CFHO + CF_3CFHO_2 \rightarrow products$$
 (7)

$$CF_3O_2 + CF_3CFHO_2 \rightarrow CF_3O + CF_3CFHO + O_2$$
 (8)

These are necessary, at low and moderate/high temperatures, respectively, to model correctly the observed decay of CF_3CFHO_2 radicals, as discussed below. Finally, the self-reaction

$$CF_3O_2 + CF_3O_2 \rightarrow \text{products}$$
 (9)

accounts for the disappearance of the UV absorption by the reaction mixture at long times. The rate constants used in this

reaction ^a	rate const at 297 K
$1a, CF_3CFHO_2 + CF_3CFHO_2 \rightarrow$	$k = 6.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1 b}$
$2CF_3CFHO + O_2$	
1b, $CF_3CFHO_2 + CF_3CFHO_2 \rightarrow$	$k = 1.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$CF_3COF + CF_3CFHOH + O_2$	
2a, $CF_3CFHO \rightarrow CF_3 + HC(O)F$	$k = 2 \times 10^4 \mathrm{s}^{-1 b}$
7, CF ₃ CFHO + CF ₃ CFHO ₂ \rightarrow	$k = 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1 b}$
products	(≤238 K)
3, $CF_3 + O_2 + M \rightarrow CF_3O_2 + M$	$k = 6.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1.11}$
8, CF ₁ CFHO ₂ + CF ₁ O ₂ \rightarrow CF ₁ CFHO	$k = 8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1 b}$
$+$ $CF_{1}O + O_{2}$	
9, $CF_3O_2 + CF_3O_2 \rightarrow \text{products}$	$k_{\rm obs} = 3.1 \times 10^{-12} {\rm cm}^3 {\rm s}^{-1.0,11}$

^aReaction numbers correspond to those used in the text. ^b Measured in the present study.



Figure 6. Concentration vs time profiles of CF_3CFHO_2 and CF_3O_2 at 297 K. The dashed curves show the effect of a ±14% change in self-reaction rate constant on the predicted change in species concentration vs time. The dot-dash curve illustrates the predictions for a simple second-order decay of CF_3CFHO_2 .

paper with respect to reaction 9 refer to the observed disappearance of CF_3O_2 . Omitted from Table II are reactions involving the CF_3O radical which is produced by this reaction. As discussed in ref 11, the reactions of CF_3O are important with respect to understanding the chemistry of the CF_3O_2 self-reaction and in interpreting the observed rate constant. However, CF_3O is produced too late and too slowly to be significantly involved with the CF_3CFHO_2 self-reaction.

B. Determination of Rate Constants. A quantitative measurement of the concentration of the UV absorbing species in the reaction mixture as a function of time is obtained by comparing the absorbance at time t with reference spectra of the species under investigation; thus, for T > 238 K

Abs (t) =

$$[CF_{3}CFHO_{2}](t)l\sigma(CF_{3}CFHO_{2}) + [CF_{3}O_{2}](t)l\sigma(CF_{3}O_{2})$$
(10)

where l represents the path length and σ the reference cross sections. At temperatures below 238 K, eq 10 is augmented with a third term to account for CF₃CFHO. The desired time-dependent concentrations are extracted via a two- (or three-)parameter least-squares fit of the time-resolved spectra to the reference spectra. The absorption cross sections used in the fitting procedure are provided in Table I.

The decay of CF₃CFHO₂ and concomitant production of CF₃O₂ at room temperature are shown in Figure 6. There are three points worth noting. The first concerns the rate of disappearance of CF₃CFHO₂. The dot-dash curve represents the predictions from a second-order rate law. Clearly, the CF₃CFHO₂ decays too rapidly at long times to be consistent with this rate law. The enhanced decay rate can be explained by reactions 2a, 3, and 8 which, while removing CF₃CFHO₂ radicals, maintain at a constant level the population of peroxy radicals with which CF₃CFHO₂ can react. When these reactions are incorporated into the model, the solid line for the CF₃CFHO₂ decay is obtained based on a



Figure 7. Concentration vs time profiles for CF_3CFHO_2 and CF_3O_2 at 363 K.



Figure 8. Concentration vs time profiles for CF_3CFHO_2 , CF_3CFHO , and CF_3O_2 at 216 K.

TABLE III: Rate Constants^a vs Temperature

<i>T</i> , K	\boldsymbol{k}_1	k _{2a}	k 7	k ₈	<i>k</i> ,	
211	15 ± 2.1					
216	12 ± 1.7	1 ± 0.5	5±3	12 ± 12	8 ± 8	
223	12 ± 1.7	1.5 ± 0.75	5 ± 3	11 ± 11	8 ± 8	
223	11 ± 1.5					
238	10 ± 1.4	3 ± 1.5	5 ± 3	10 ± 7	4 ± 3	
238	9 ± 1.4					
254	9 ± 1.4	10 ± 4		10 ± 5	4 ± 2	
297	7 ± 1.0	20 ± 10		8 ± 3	3 ± 0.8	
323	5 ± 0.7	50 ± 15		6 ± 3	3 ± 1	
363	4 ± 0.6	70 ± 15		5 ± 3	2.6 ± 1	
372	3.7 ± 0.5	85 ± 20		5 ± 3	2.6 ± 1	

^a Units are 10^{-12} cm³ s⁻¹, except for k_{2a} which has units of 10^3 s⁻¹.

rate constant of $k_{1a} + k_{1b} = (7 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for the sum of reactions 1a and 1b, an 0.84/0.16 branching ratio, a 2 × 10⁴ s⁻¹ CF₃CFHO decay rate, and a rate constant of $k_8 = (8 \pm 3) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for the mixed peroxy radical reaction.¹⁸

The second point is somewhat more subtle. A careful examination reveals that the rate of rise in the CF₃O₂ concentration lags the rate of decay in CF₃CFHO₂. Scrutiny of Figures 7 and 8 shows that the lag time becomes shorter at high temperatures and much longer at low temperatures. These observations are indicative of the fact that CF₃O₂ is not a direct product of the CF₃CFHO₂ reaction, in accord with our observation of CF₃CFHO production at low temperatures and the mechanism deduced from the FTIR studies of Wallington et al.⁸ At room temperature, a rate of $k_{2a} = (2 \pm 1) \times 10^4 \text{ s}^{-1}$ for the alkoxy radical decomposition gives a good fit to the observed rise of CF₃O₂ in Figure 6 (solid line).

The third point concerns the rate of CF_3O_2 decay. The observed disappearance of this species in the present experiments is consistent with the value of $k_{9obs} = 3.1 \times 10^{-12}$ cm³ s⁻¹ measured in our previous work.¹¹ The solid curve¹⁸ through the CF_3O_2 data in Figure 6 is based on this value of the rate constant.



Figure 9. Temperature dependence of the CF_3CFHO_2 self-reaction rate constant. The line represents the best fit of the data to an Arrhenius expression.

The estimates of errors in the rate constants reported above and in Table III are based on the sensitivity of the predicted concentration vs time curves to various rate constants. The dotted curves in Figure 6 show the effect of a 14% variation in k_1 on the predicted CF₃CFHO₂ concentrations. It is apparent that the CF₃CFHO₂ decay is the most sensitive to this parameter, as expected, and that this variation in k_1 gives a reasonable accounting of the scatter in the data. Conversely, the long time decay of CF₃O₂ is nearly independent of k_1 over the ±14% range.

Similar tests were carried out for the other rate constants. Thus, a 50% variation in CF3CFHO decomposition rate has a large effect on the CF_3O_2 rise time but a small-to-negligible effect on either the CF_3CFHO_2 decay rate or the long-time CF_3O_2 decay. A change of $\pm 3 \times 10^{-12}$ cm³ s⁻¹ in k_8 only affects the long time $(>500-\mu s)$ decays of CF₃CFHO₂ and CF₃O₂ and accounts for the scatter of data at these times. This error bar is larger than that of k_1 because the parameter is determined primarily from the data for the concentration of CF₃CFHO₂ at long times, which are small and therefore more susceptible to noise and systematic errors. Finally, changes in k_{9obs} affect only the long time decay of CF₃O₂. A variation of about 30% adequately covers the scatter in the data at moderate and high temperatures. As the temperature is lowered below 273 K, the error in the CF₃O₂ observed self-reaction rate becomes increasingly larger because of the progressively smaller amount of this radical produced.

C. Temperature Dependence. A qualitative view of the temperature dependence of the CF_3CFHO_2 self-reaction, and the subsequent reactions, can be obtained from a comparison of Figures 6-8. Upon increasing the reaction temperature to 363 K, the rate of CF_3CFHO_2 decay decreases. Conversely, cooling the reaction of 216 K produces nearly a factor of 2 increase in the self-reaction rate constant compared to its room-temperature value. At 363 K, the appearance of CF_3O_2 nearly coincides with the loss of CF_3CFHO_2 over the first millisecond of reaction. In stark contrast, CF_3O_2 appears only very slowly at T = 216 K; rather, it is the appearance of CF_3CFHO that closely follows the loss of CF_3CFHO_2 radicals.

The variation of the CF₃CFHO₂ rate constant with temperature is shown in Figure 9 and listed in Table III. The data reveal a moderate negative temperature dependence, with a 4-fold decrease in the rate constant over the temperature range of 211-372 K. Within the scatter of the data, the temperature dependence is well fit by an Arrhenius expression

$$k = A \exp(-T^*/T) \tag{11}$$

having a negative activation energy, $T^* = -605 \pm 40$ K, and a preexponential factor of A (7.8 \pm 1.3) \times 10⁻¹³ cm³ s⁻¹.

The dependence of the CF₃CFHO decomposition rate on temperature is illustrated in Figure 10 and in Table III. Between 216 and 372 K, the rate increases by almost 2 orders of magnitude. These data, too, are well fit by eq 11, with $T^* = 2200 \pm 150$ K and $A = (3.7 \pm 0.7) \times 10^7$ s⁻¹. The pressure-dependent study of k_{2a}/k_{2b} by Wallington et al.⁸ shows that the reaction does not



Figure 10. Temperature dependence of the CF_3CFHO dissociation at 230 Torr. The solid line is a best fit of the data to an Arrhenius expression.

reach its high-pressure limit until approximately 2 atm of total pressure. Therefore, at the 230-Torr total pressure of the present experiments, T^* does not represent the potential barrier for the dissociation of CF₃CFHO; rather it represents the composite temperature dependence due to the dissociation barrier and to the collisional excitation of the alkoxy radical.

The temperature-dependent rate constants for reactions 8 and 9 are also reported in Table III. Both reaction rates increase with decreasing temperature. In view of the qualitative nature of these rate constants, however, no effort was made to fit them to eq 11 or other expressions.

D. Discussion. The self-reaction of CF_3CFHO_2 is comparatively fast. At 297 K, it proceeds at approximately 20 times the rate of the self-reaction of CH_3O_2 and is nearly 2 orders of magnitude faster than the $C_2H_5O_2$ self-reaction,^{14,19} indicating a significant effect on the reaction dynamics from fluorine substitution. While not universal, the observation of a negative temperature dependence for peroxy radical self-reactions is not unusual. In the case of ethyl peroxy radical, the temperature dependence is positive; however, the methyl peroxy radical selfreaction rate increases with decreasing temperature.^{14,19} Furthermore, a number of other chlorine-, fluorine-, and OH-substituted ethyl and methyl peroxy radicals exhibit a negative temperature dependence for self-reaction with T^* in the range of -500 to -1000 K.¹⁴ A common, though not universal, correlation exists between a relatively rapid self-reaction rate and a negative temperature dependence. A possible explanation is that the self-reaction proceeds via dimer formation followed by decomposition of the dimer into the various product channels. As the decomposition rate increases, the rate of dimer formation becomes the limiting step in the overall reaction; thus, with dimer formation becoming more favorable as the temperature is lowered, fast reactions will tend to exhibit a negative temperature dependence.

With one exception, the kinetic model posited in Table II is consistent with the time-resolved UV spectra recorded in the present study and with the previous FTIR product study of HFC-134a photooxidation. This concerns the temperature dependence of the branching ratio for reactions 1a and 1b. The UV data are not sensitive to the products of reaction 1b; however, the yield of reaction 1a can be deduced from the amount of CF_3O_2 that is formed, although the latter depends also on the rate constants for its formation and subsequent reactions. For our room-temperature data, we set the branching ratio of reactions 1a and 1b to the value reported by Wallington et al.,⁸ namely, 0.84 for channel 1a and 0.16 for channel 1b, and obtained very good agreement (Figure 6) between the measured concentration vs time profiles for CF_3CFHO_2 and CF_3O_2 profiles and the predictions based on the kinetic model listed in Table II.

As we varied the temperature, a good fit between the concentration vs timed data and the model predictions could be maintained by decreasing k_1 and increasing k_{2a} with increasing temperature, making small adjustments to k_8 and k_9 but keeping the branching ratio fixed at its room-temperature value. Over the temperature range 273-363 K, this assumption of a constant branching ratio is consistent with Wallington et al.⁸ They obtain $k_{1a}/k_{1b} = 0.9/0.1, 0.84/0.16, \text{ and } 0.72/0.28 \text{ for } 353, 297, \text{ and}$ 273 K, respectively.

The discrepancy arises when one attempts to extrapolate the three temperature measurements of ref 8 to 216 K. Our timeresolved UV data remain consistent with the assumption that the branching ratio of reactions 1a and 1b stays near its room temperature value; in contrast, the extrapolation would predict that the ratio changes to $k_{1a}/k_{1b} = 0.22/0.78$ at 216 K. There are two pieces of evidence which suggest that k_{1a}/k_{1b} may be closer to 0.84/0.16 than to 0.22/0.78 at 216 K. The data in Figure 8 show that the maximum level of CF₃O₂ produced on account of the CF₃CFHO₂ self-reaction is much lower at 216 K than at 297 K or 363 K, Figures 6 and 7, respectively. This in itself would be consistent with a lower yield of reaction 1a relative to reaction 1b. However, there is also a considerable delay in the formation of CF_3O_2 , which coupled with the additional spectral feature, attributed to CF₃CFHO, suggests that the formation of CF₃O₂ is limited by the decomposition of the alkoxy radical. The observed level of CF_3O_2 is consistent either with a reduction in k_{2a} or with a decrease in k_{1a}/kl_{b} , but not both. Because of the appearance of CF₃CFHO at low temperatures, we believe the former to be the more likely explanation for the low level of CF_3O_2 . The second piece of evidence has to do with the departure from second-order kinetics at long times for reaction 1. This requires that a product of the CF₃CFHO₂ self-reaction react with the parent radical, an unlikely event if channel 1b dominates.

Finally, we can combine the present measurement of the alkoxy radical decomposition rate with the relative rate measurement of Wallington et al.⁸ in order to determine the rate constant for the $CF_3CFHO + O_2$ reaction. The latter authors have determined that $k_{2a}/k_{2b} = 1.5 \times 10^{19} \text{ cm}^{-3}$ at 297 K and 230 Torr of total pressure; therefore, $k_{2b} = 1.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ at 297 K. This reaction is, therefore, somewhat slower than the analogous reaction of ethoxy radical with O_2 , for which rate constants in the range of 8×10^{-15} to 1.1×10^{-14} cm³ s⁻¹ have been reported.

V. Conclusion

We have used the technique of laser flash photolysis-timeresolved UV spectroscopy to measure the UV spectrum and investigate the self-reaction kinetics of the CF₃CFHO₂ peroxy radical. The UV spectrum of CF₃CFHO₂ is characteristic of peroxy radicals; the absorption is broad and featureless, with a maximum intensity of $(5.2 \pm 0.3) \times 10^{-18}$ cm² molecule⁻¹ at 213 nm. This spectrum is in good agreement with the previous work of Wallington and Nielsen⁶ but is approximately 35% more intense than the spectrum reported by Jemi-Alade et al.⁷

The time-resolved spectra show that, as the CF₃CFHO₂ decays via reaction, CF_3O_2 is formed. This is consistent with the FTIR product study of ref 8 and presumably occurs via decomposition of the alkoxy radical formed by the CF₃CFHO₂ self-reaction. As the temperature is lowered below 240 K, a third species appears in the UV spectra. This feature, in the region of 260-280 nm,

becomes more prominent as the temperature is further reduced and, concurrently, the level of CF_3O_2 formation dramatically decreases. Accordingly, it is assigned to the alkoxy radical CF₃CFHO.

With a rate constant of $k_1 = 7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, the CF₃CFHO₂ self-reaction is relatively fast. It has a moderate negative temperature dependence, a characteristic not uncommon of peroxy radicals. The fate of the CF₃CFHO produced via the self-reaction is of atmospheric importance with regard to the degradation of HFC-134a, because the same alkoxy radical is produced from the reaction of CF₃CFHO₂ with NO.⁶ We have measured the temperature-dependent decomposition of CF₃CFHO into CF₃ and HFCO and deduced, using relative rate data, the rate constant for the reaction of CF₃CFHO with molecular oxygen.

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