Relative Rate and Product Studies of the Reactions of Atomic Chlorine with Tetrafluoroethylene, 1,2-Dichloro-1,2-difluoroethylene, 1,1-Dichloro-2,2-difluoroethylene, and Hexafluoro-1,3-butadiene in the Presence of Oxygen

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S Supporting Information

ABSTRACT: Rate coefficients k_1 – k_3 have been measured for Cl atom reactions with $\text{CF}_2=\text{CF}_2$, $\text{CFCl}=\text{CFCl}$, and $\text{CCl}_2=\text{CF}_2$ relative to k_4 for $\text{CF}_2=\text{CF}=\text{CF}=\text{CF}_2$ at 293 ± 2 K. k_4 was remeasured relative to Cl + ethane. Cl was generated by UV photolysis of Cl_2 , and other species were monitored by FT-IR spectroscopy. The measurements yield $k_1 = (6.6 \pm 1.0) \times 10^{-11}$, $k_2 = (6.5 \pm 1.0) \times 10^{-11}$, and $k_3 = (7.1 \pm 1.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, and $k_4 = (8.0 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is proposed. These results are discussed in the context of atmospheric chemistry. Subsequent chemistry in the presence of oxygen leads to oxygenated products that are identified via their IR spectra, and possible mechanisms are discussed. The yield of CF_2O from C_2F_4 is $93 \pm 7\%$. Dichlorofluoroacetyl fluoride (CCl_2FCFO) was observed as a product from $\text{CFCl}=\text{CFCl}$, and chlorodifluoroacetyl chloride (CClF_2CClO) was observed from $\text{CCl}_2=\text{CF}_2$ oxidation. C_4F_6 led to $66 \pm 5\%$ CF_2O and $38 \pm 3\%$ $\text{OCF}_2\text{CFC(F)=O}$. Reaction enthalpies and enthalpy barriers computed via CBS-QB3 theory help rule out some unfavorable mechanistic steps.

1. INTRODUCTION

The Montreal Protocol on Substances that Deplete the Ozone Layer of 1987 addressed the emission of chlorofluorocarbon (CFC) molecules into the atmosphere where, because of their slow reactions with typical tropospheric radicals such as Cl, OH, and HO_2 , they survive long enough to be transported to the stratospheric ozone layer where they are photolyzed by short-wavelength UV. The resulting Cl atoms catalyze removal of odd oxygen.^{1,2} Accordingly, CFCs have for many uses been replaced by hydrofluorocarbons (HFCs), which have little ozone depletion potential because of the lack of chlorine. However, their C–H bonds react slowly with OH, and the consequential long atmospheric lifetimes combined with strong infrared (IR) absorption in spectral regions not saturated by CO_2 absorption lead to very high global warming potentials (GWPs) for HFCs. A context for the work here is exploration of the possibility of employing substitute molecules that contain carbon–carbon π bonds that introduce a highly reactive site, so that these molecules may be rapidly scavenged from the atmosphere. Such halo-olefin species have GWPs around 3 orders of magnitude smaller than those of HFCs and have recently been highlighted as practical propellants for aerosol cans and working fluids for refrigeration.^{3,4}

We have made measurements of the rates of the reactions

relative to the reference compound perfluorobutadiene, $\text{CF}_2=\text{CF}=\text{CF}=\text{CF}_2$, whose absolute rate constant is known at room temperature.⁵ These data permit assessment of their atmospheric lifetime with respect to consumption by Cl, which is most relevant to regions where [Cl] is highest, notably the marine boundary layer (MBL).⁶ The first reaction has not been studied before, and these systems may serve as models that reveal fundamental chemistry that underlies the behavior of larger systems. For all three reactions, our observations of product formation in the presence of oxygen also indicate some of the subsequent fate of these species in the atmosphere and also that for C_4F_6 .

2. METHODOLOGY

Commercial samples of hexafluoro-1,3-butadiene ($\text{CF}_2=\text{CF}=\text{CF}=\text{CF}_2$, Air Liquide), a mixture of *E* and *Z* isomers of ($\text{CFCl}=\text{CFCl}$) (Matrix Scientific, 99%) and $\text{CCl}_2=\text{CF}_2$ (Synquest, 90%) were used. We synthesized a few torr of pressure of C_2F_4 by pyrolysis of PTFE under vacuum⁷ [CAUTION: high pressures of C_2F_4 can polymerize explosively]. These reagents, and chlorine (Matheson, 99.9%), were purified by repeated freeze–pump–thaw cycles

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with liquid nitrogen. The general principles of relative rate measurements are well-established.⁸ In brief, for the present application, molecular chlorine was photolyzed by steady illumination from a mercury lamp in the presence of the reactant olefin and a reference compound. The reference was a molecule whose absolute rate constant for reaction with atomic Cl was already known. Consumption of the reactant and reference was monitored by infrared spectroscopy, and the relative loss rate was determined, which yielded the ratio of the rate constants for reaction with Cl.

We have assembled a new apparatus where chemistry occurs at room temperature within a Pyrex multipass cell with a 2.4 m path length (IR Analysis 2.4-PA). The volume is 100 cm³. Prior to each experiment, the cell was evacuated to about 50 mbar and filled with a manometrically prepared mixture of typically around 0.1 mbar of reference compound, around 0.1 mbar of reactant, 0.2–1 mbar of Cl₂, and 930 mbar of Ar (Air Liquide, 99.9995%). For each reactant, we verified that photolysis in the absence of Cl₂ and storage in the dark with Cl₂ did not cause any reaction. The cell was mounted inside of a Fourier Transform IR spectrometer (Nicolet iS50) with a mercury cadmium telluride detector cooled with liquid nitrogen, and the UV source was a Pen-Ray 11SC-2.12 lamp with a quartz envelope, supported 2.5 cm from one side of the infrared cell. This lamp has strong emission in the regions of 184, 254, and 365 nm; the Pyrex walls of the cell are expected to block the first two regions. On the basis of the manufacturer's specifications, the UV intensity at the center of the cell at 365 nm is about 30 mW cm⁻². During photolysis, typically 10 spectra were recorded at a rate of 1/min, each with 82 co-added scans at 2 cm⁻¹ resolution. Distinctive peaks in the infrared spectra of the reactant and reference were selected, and the integrated absorbance over the band was evaluated. The concentrations employed correspond to absorbances (base 10) below 1.0 so that Beer–Lambert behavior is expected and the absorbance is proportional to concentration. This was verified in the case of C₄F₆, whose absorbance was checked as a function of the partial pressure of C₄F₆.

With the important assumption that the dominant loss mechanism for both the reactant and the reference is reaction with atomic chlorine, the following reaction scheme can be analyzed:

The products of steps 5 and 6 are radicals that may in turn react with Cl₂ to regenerate Cl atoms. In preliminary tests with ethane/Cl₂ mixtures, an essentially exponential decay of [C₂H₆] was observed, whose decay constant corresponded to a steady-state concentration [Cl] on the order of 10⁷ atom cm⁻³. Ethyl radicals formed from Cl + C₂H₆ likely regenerate Cl atoms via C₂H₅ + Cl₂. This means that because [Cl] is approximately constant step 7 is seen to balance step 4. Given that homogeneous Cl + Cl recombination is very slow, we conclude that wall losses of Cl offset its formation via photolysis. We imagine that the inner surface of the cell and the gold mirrors catalytically recombine the Cl atoms. This is significant because otherwise the overall radical concentrations and reaction rates would increase without limit under steady UV illumination.

With a diffusion coefficient for Cl of 0.19 cm² s⁻¹ at 1 atm⁹ and treating the cell as a cylinder 11.5 cm long with a diameter of 3.3 cm, we estimate^{10,11} an effective first-order rate constant of 2.4 s⁻¹ for diffusion loss of Cl from the long-time solution to the diffusion equation. Because this value is 4 orders of magnitude higher than the observed loss rate (which also includes any reaction of Cl with impurities such as hydrocarbons in the bath gas), we deduce that the probability of Cl sticking in an individual collision with the walls is extremely low. We also note that a bulk diffusion time scale of seconds ensures homogeneity in the mixture during the kinetic experiments, which take place on a time scale of minutes.

The rate of step 5 is $k_{\text{R}}[\text{Cl}][\text{reactant}]$ so that we may write

$$-d \ln[\text{reactant}]/dt = k_{\text{R}}[\text{Cl}] \quad (8)$$

Similarly for step 6

$$-d \ln[\text{reference}]/dt = k_{\text{ref}}[\text{Cl}] \quad (9)$$

Integration of the ratio of expressions 8 and 9 yields the standard result⁸ (where the subscript 0 refers to the initial value and t to a later time)

$$\ln \left\{ \frac{[\text{reactant}]_0}{[\text{reactant}]_t} \right\} = \frac{k_{\text{R}}}{k_{\text{ref}}} \ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} \quad (10)$$

which is true even if a steady-state [Cl] is not established or if pseudo-first-order conditions do not hold. In fact, they do here. The ratios of concentrations were determined from the ratios of absorbances. We employed C₄F₆ as the reference compound, for which Wallington and Hurley⁵ have determined, in two runs relative to Cl + acetylene and ethylene, $k_{\text{ref}} = (6.86 \pm 0.57) \times 10^{-11}$ and $(7.70 \pm 0.55) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, respectively. We redetermined k_{ref} with two runs relative to Cl + ethane (for which the rate constant is 5.7×10^{-11} cm³ molecule⁻¹ s⁻¹)¹² and obtained ratios of 1.473 ± 0.018 and 1.429 ± 0.032 , which yield $k_{\text{ref}} = (8.40 \pm 0.29)$ and $(8.15 \pm 0.41) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Combination of these four determinations of k_{ref} yields a weighted mean value (as outlined by Bevington¹³) of 8.0×10^{-11} cm³ molecule⁻¹ s⁻¹. Twice the standard deviation of the mean is 0.4×10^{-11} cm³ molecule⁻¹ s⁻¹. However, given that the spread between the individual determinations might indicate that systematic errors are present, we prefer a more conservative confidence interval of $\pm 1.2 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for k_{ref} because this range encompasses all of the measurements.

3. RESULTS AND DISCUSSION

Figure 1 shows example plots of $\ln\{[\text{reactant}]_0/[\text{reactant}]_t\}$ vs $\ln\{[\text{reference}]_0/[\text{reference}]_t\}$, whose slope is $k_{\text{R}}/k_{\text{ref}}$ for the three systems R = C₂F₄, (E/Z)-CFCl=CFCl, and CCl₂=CF₂. Table 1 lists the experimental conditions for determinations of k_{R} via eq 10, including the initial concentrations of the reactant and reference, the spectral regions used to assess concentration, and the observed slope of a plot like Figure 1 together with its statistical uncertainty. Table 2 summarizes absolute values of k_{R} obtained by multiplying $k_{\text{R}}/k_{\text{ref}}$ by the value of k_{ref} derived above. Each experiment was repeated, and the final result for each reactant was obtained as a weighted mean of the two measurements. The uncertainty quoted here is 2σ in the $k_{\text{R}}/k_{\text{ref}}$ ratio combined in quadrature with 3% for possible propagated systematic errors in concentration and temperature and the error limit for the reference compound⁵ proposed above of 15%. This latter term is dominant so that

Figure 1. Concentration ratios of reactants vs the reference compound C_4F_6 , from top to bottom for the reactions $Cl + C_2F_4$, $Cl + (E/Z)-CFCFCl$, and $Cl + CCl_2CF_2$.

the effective uncertainty in all of the rate constants is 15%. We now discuss each reactant individually.

3.1. Rate Constant and Oxidation Products of C_2F_4 . The rate constant for reaction 1 has not been determined previously, but our result of $(6.6 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is comparable to those known for other halogenated alkenes, including C_4F_6 ⁵ which are typically around $(5\text{--}10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For a tropospheric daily average $[Cl]$ of $3 \times 10^4 \text{ molecules cm}^{-3}$,¹⁴ the lifetime of C_2F_4 with respect to reaction with Cl is about 6 days. Because hydroxyl is 6 times less reactive toward C_2F_4 ¹⁵ but about 30

Table 2. Summary of the Absolute Rate Constants for Fluorocarbon Reactions with Cl Atoms at Room Temperature

fluorocarbon	$k \pm 2\sigma / 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
$CF_2=CF_2$	6.51 ± 0.18
	6.66 ± 0.14
	6.56 ± 0.98^a
$CFCl=CFCl$	6.60 ± 0.31
	6.43 ± 0.29
	6.51 ± 0.98^a
$CCl_2=CF_2$	7.33 ± 0.16
	7.09 ± 0.07
	7.12 ± 1.07^a

^aWeighted mean with 15% uncertainty propagated from the uncertainty in k_{ref} (see the text).

times more abundant,¹⁶ consumption by OH will be about 5 times faster. However, in the MBL where $[Cl]$ peaks in the range of $(1\text{--}3) \times 10^5 \text{ molecules cm}^{-3}$,^{17,18} reaction 1 may dominate and can lead to lifetimes for C_2F_4 as short as ~ 0.6 days. The precise magnitude of this short time will be sensitive to mixing, local conditions, and the time of day, but even this rough estimate indicates that the GWP of C_2F_4 is negligible.

In our experiments, it proved impossible to remove all traces of oxygen, and the minimum pressure attained was 50 mbar (which is the specified performance of the multipass IR cell). The time history of the IR spectra showed consumption of C_2F_4 , of course, and the only other species noted was CF_2O ¹⁹ as its concentration increased. Initial and final spectra for an irradiated $C_2F_4/Cl_2/O_2$ mixture are shown in Figure 2. We did not observe CF_2ClCF_2Cl , which would be expected from reaction of the initial $Cl + C_2F_4$ adduct with Cl_2 . There must therefore be fast competing chemistry that cleaves the carbon atoms at room temperature, overcoming the C–C bond dissociation enthalpy of $D_{298} \approx 295 \text{ kJ mol}^{-1}$.²⁰

In another experiment, we used this photochemical reaction to prepare CF_2O , separated it by low-temperature distillation, and calibrated the integrated IR intensity with a known partial pressure of CF_2O in the IR cell. Propagation of reasonable experimental uncertainties suggests that this calibration is accurate to $\sim 5\%$. When two different species are compared, ratios are likely accurate to about 7%. Given our calibration, we deduce that $93 \pm 7\%$ of the consumed C_2F_4 is transformed to CF_2O .

We propose the following mechanism, where the reaction enthalpies at 298 K have been computed via the CBS-QB3 computational methodology.²¹ This incorporates approximate extrapolation of coupled cluster results to the complete basis set limit, at geometries determined with density functional theory (DFT), namely, B3LYP used with the 6-311G(2d,d,p) atomic basis set. This level of DFT is also used for harmonic

Table 1. Initial Concentration of the Reactants, Integrated Spectral Regions, and Rate Coefficient Ratios (k_R/k_{ref}) for the Reactions of Cl Radicals with Three Reactants R Relative to the Reference C_4F_6 at $(293 \pm 2) \text{ K}$

reactant	$[R]_0 / 10^{15} \text{ molecules cm}^{-3}$	integrated range/ cm^{-1}	$[ref]_0 / 10^{15} \text{ molecules cm}^{-3}$	integrated range/ cm^{-1}	$(k_R/k_{\text{ref}}) \pm \sigma$
$CF_2=CF_2$	2.77	1167–1200	2.63	1312–1363	0.813 ± 0.011
	2.05		1.95		0.832 ± 0.009
$(E/Z)-CFCFCl$	2.34	1155–1180	2.90		0.826 ± 0.019
	1.79		2.23		0.803 ± 0.018
$CF_2=CCl_2$	2.68	1110–1150	1.95		0.916 ± 0.010
	2.14		1.56		0.886 ± 0.004

Figure 2. Initial and final infrared spectra for photolysis of a $\text{Cl}_2/\text{C}_2\text{F}_4$ mixture in the presence of O_2 . Absorbance is base 10.

vibrational analysis and thermal corrections. These calculations were carried out with the Gaussian 09 program suite,²² and the computed structures and energies are provided in the [Supporting Information](#). CBS-QB3 is not highly accurate, and we expect errors up to around 10 kJ mol^{-1} , but this method provides an approximate assessment of enthalpies and barrier heights that are otherwise unavailable, including for the larger species considered below. In some cases, barrier heights are derived via searches for the saddle point along the reaction coordinate connecting the specified reactants and products. The geometry at this transition state (TS) is confirmed by visualization of the imaginary frequency that corresponds to motion along the reaction coordinate and in ambiguous cases is followed up by computation of the intrinsic reaction coordinate starting from the TS. The enthalpy at the TS relative to the reactants yields the barrier, which we evaluate here for 298 K. The observed activation energy for a bimolecular reaction is typically larger by about $2RT$. We comment that to be significant in atmospheric chemistry, which occurs at room temperature and below, proposed bimolecular reaction pathways cannot be significantly endothermic, and any barriers must be modest or negligible.

The initial step is addition of Cl to the π bond

followed by addition of oxygen

We envisage two possible fates for this peroxy radical

The self-reaction of peroxy radicals is well-known, and at the high concentrations encountered in laboratory studies, [reaction 13](#) is likely. The analogous self-reaction for CF_3OO has a rate constant²³ of $2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and we speculate that the rate constant for [reaction 13](#) is similar. It is not expected to be important in the atmosphere, where the concentration of peroxy species will be much smaller than that in the laboratory experiments. An alternative path to the halogenated ethoxy species is O atom abstraction by a radical as in [reaction 14](#). In our experiments, this may be carried out by Cl atoms, while in the atmosphere, NO is typically invoked for this role.⁴ As a specific example, the reactions of CF_3OO with Cl and NO have rate constants of about 4×10^{-11} and $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, at room temperature,²⁴ which are within a factor of 10 of the collision rate so that any barriers are small. Driven by the high stability of CF_2O , the product ethoxy could dissociate

Here the negative reaction enthalpy indicates that the halogenated ethoxy radical is metastable, by contrast to hydrocarbon alkoxy radicals. Our computations predict a long C–C bond in this haloethoxy species, $1.62 \times 10^{-10} \text{ m}$, and a barrier to dissociation was located via DFT at a C–C separation of $1.87 \times 10^{-10} \text{ m}$. The enthalpy barrier at 298 K relative to $\text{CF}_2\text{ClCF}_2\text{O}$ is 9 kJ mol^{-1} via the CBS-QB3 method. This low barrier implies a high rate constant for [reaction 15](#). Indeed, dissociation could be concerted with [reactions 13](#) or [14](#).

The subsequent fate of CF_2Cl is rapid reaction with O_2 , which has been studied in detail by Codnia and Azcárate.²⁵ There are two channels that at 298 K and 1 bar contribute approximately equally

The CF_2ClOO peroxy species may react analogously to $\text{CF}_2\text{ClCF}_2\text{OO}^\bullet$, that is, via

The endothermicity of [reaction 18](#) suggests that [reaction 19](#) may be the dominant path, unless the self-reaction is concerted with exothermic Cl-atom elimination

Our calculations indicate that the TS for reaction 20 is at a C–Cl distance of 2.01×10^{-10} m. The 298 K enthalpy barrier to dissociation computed at this geometry is -26 kJ mol^{-1} (CBS-QB3). Whether CF_2ClO is metastable or in fact unstable, clearly it will dissociate rapidly. Overall, therefore, reactions 11–20 provide a fast pathway for the overall Cl-atom-catalyzed oxidation of C_2F_4

3.2. Rate Constant and Oxidation Products of (E/Z)-CFCI=CFCl. The mixture of isomers was monitored via absorbance in the region of $1150\text{--}1180 \text{ cm}^{-1}$, which is common to both species.²⁶ There are two minor unique peaks, but one is obscured by the absorption spectra of the products (see Figure 3), and therefore, it was not possible to

Figure 3. Initial and final infrared spectra for photolysis of a $\text{Cl}_2/\text{CFCI=CFCl}$ mixture in the presence of O_2 . Absorbance is base 10.

resolve the kinetics of individual cis or trans isomers. We dissolved some of our CFCI=CFCl in $\text{CDCl}_3(\text{l})$ and used ^{19}F NMR²⁷ to determine an initial composition of $51 \pm 2\%$ cis isomer. The effective overall rate constant for reaction of this mixture with Cl is $k_2 = (6.5 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, very similar to that for C_2F_4 and in accord with the value of $(5.4 \pm 1.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained recently by Barrera et al.²⁸ Similar remarks therefore apply to the atmospheric lifetime with respect to reaction 2. This lifetime will be even shorter in the presence of hydroxyl, but it is already clear that the GWP is minor. We observed dichlorofluoroacetyl fluoride (CCl_2FCOF) in the product spectrum in Figure 3B, assigned by comparison with the published spectrum.²⁹

Reaction 2 may also lead to COFCl whose spectrum,³⁰ if it is present in modest quantities, would be largely overlapped. COFCl could be formed analogously to the mechanism proposed above for C_2F_4 , but Sanhueza and Heicklen, who conducted similar experiments to ours by photolyzing $\text{Cl}_2/\text{O}_2/\text{CFCI=CFCl}$ mixtures,³¹ reported no formation of COFCl and instead assigned CFCI_2CFO as the exclusive product. A question therefore is why is this reaction different from reaction 1? We have analyzed two potential decomposition pathways of the likely intermediate

At the CBS-QB3 level of theory, the reaction enthalpies indicate that the halogenated ethoxy intermediate is metastable with respect to both pathways. Accordingly, we characterized the TSs. The enthalpy barriers at 298 K are 22 and 6 kJ mol^{-1} , respectively, for reactions 22 and 23, and therefore, kinetic control of the decomposition of the ethoxy intermediate favors loss of the Cl atom and formation of the observed CCl_2FCFO .

In the absence of oxygen, we would expect the product to be $\text{CFCI}_2\text{CFCI}_2$ (CFC-112) from interception of the initial $\text{CFCI}_2\text{CFCI}^\bullet$ radical by Cl_2 rather than by O_2 . The integrated absorption cross section of CFC-112 was published by Oliff and Fischer in 1994, but not the spectrum. In 2014, Etminan et al.³² examined the spectrum at high resolution but were unable to obtain a pure sample. We synthesized CFC-112 via 4 h of photolysis of a mixture of 10 mbar of Cl_2 and 0.7 mbar of CFCI=CFCl , followed by freeze–pump–thaw purification at 77 K and distillation from 273 K. The spectrum is shown in Figure 4. The main difference from the Etminan et al. spectrum of a mixture of CFC-112 and CFC-112a is the absence of their peak at 1170 cm^{-1} . The likely impact on the calculated radiative forcing is modest. While this work was in progress, a new spectrum was published by Davis et al.³³ Our spectrum is in

Figure 4. Infrared spectrum of CFC-112. The conditions were 0.4 mbar of $\text{CFCI}_2\text{CFCI}_2$ diluted in 800 mbar of Ar, 1000 scans at 0.25 cm^{-1} resolution, path length of 2.4 m, at $290 \pm 2 \text{ K}$. Absorbance is base 10.

good accord, with the same peak locations and leading to a radiative efficiency (RE) of $0.32 \text{ W m}^{-2} \text{ ppb}^{-1}$, in agreement with the value of $0.28 \text{ W m}^{-2} \text{ ppb}^{-1}$ determined by Davis et al.

3.3. Rate Constant and Oxidation Products of $\text{CCl}_2=\text{CF}_2$. Our measured rate constant is $k_3 = (7.1 \pm 1.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and therefore, reaction 3 is another example of a rate constant that is close to the hard-sphere collision value. This value agrees with the determination of $(6.3 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Barrera et al.²⁸ Infrared spectra of mixtures with Cl_2 and O_2 before and after UV photolysis are shown in Figure 5. The major product peaks are

Figure 5. Initial and final infrared spectra for photolysis of a $\text{Cl}_2/\text{CCl}_2\text{CF}_2$ mixture in the presence of O_2 . Absorbance is base 10.

assigned to chlorodifluoroacetyl chloride, CClF_2CClO .³⁴ A plausible pathway is initial Cl addition at the CF_2 end, allowing for formation of a $\text{CClF}_2\text{CCl}_2\text{OO}$ peroxy radical that is transformed to $\text{CClF}_2\text{CCl}_2\text{O}$ and forms the acetyl chloride by loss of a Cl atom.³¹ Minor peaks of COF_2 are also visible in Figure 5B, which we attribute to addition of Cl to the CCl_2 end of the molecule. This will form a radical center at the CF_2 end, and chemistry similar to that proposed for C_2F_4 can lead to COF_2 . The observed yield is $\sim 3.6\%$ of that seen from C_2F_4 , from which we deduce the ratio for attack at the Cl/F ends of $\text{CCl}_2=\text{CF}_2$ to be about 0.04:0.96. There are also small peaks from CCl_2FCFO in Figure 5B, which we attribute to reaction of CFCICFCI which from Figure 5A makes up $\sim 8\%$ of the CCl_2CF_2 sample.

3.4. Oxidation Products of $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$. Two major products were identified from the spectrum in Figure 6B. One is CF_2O , and the other is the epoxy compound $\text{OCF}_2\text{CFC}(\text{F})=\text{O}$ where the first O atom is bonded to both of the first two C atoms. This 2,3-epoxyperfluoropropionylfluoride species has been noted before in the mercury-sensitized photolysis of $\text{O}_2/\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ mixtures.³⁵ The pub-

Figure 6. Initial and final infrared spectra for photolysis of a $\text{Cl}_2/\text{C}_4\text{F}_6$ mixture in the presence of O_2 . Absorbance is base 10.

lished IR spectrum is of low resolution. Accordingly, we prepared a sample photochemically via UV photolysis for 1.5 h of a mixture of 0.7 mbar of $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$, 4 mbar of O_2 , and 1.6 mbar of Cl_2 , which was then put through freeze-pump-thaw cycles at 77 and 195 K. The spectrum is shown in Figure 7. On the basis of the IR absorbances, we estimate yields of $66 \pm 5\%$ CF_2O and $38 \pm 3\%$ $\text{OCF}_2\text{CFC}(\text{F})=\text{O}$.

We can speculate about the mechanism leading to the epoxy product. Stuckey et al.³⁵ suggested that in their mercury-sensitized $\text{O}_2/\text{C}_4\text{F}_6$ system energy was transferred first to O_2 and then to C_4F_6 , which then reacted with O_2 to yield triplet

Figure 7. Infrared spectrum of 2,3-epoxyperfluoropropionylfluoride. The conditions were 0.5 mbar of $\text{OCF}_2\text{CFC}(\text{F})\text{O}$ diluted in 270 mbar of Ar, 6000 scans at 0.5 cm^{-1} resolution, path length of 2.4 m, at $290 \pm 2 \text{ K}$. Absorbance is base 10. Impurity peaks are marked with an *.

tively and the medium-resolution spectra of two products, not previously available, are presented. CF_2 and CFCl sites appear to be more reactive than CCl_2 sites toward addition of Cl. The results show that the Cl atom kinetics alone, even before consideration of rapid removal by OH, are sufficient to ensure that these chlorofluoro ethenes have small GWPs. Accordingly, in the context of radiative forcing, they could make potential environmentally benign substitutes for current refrigerants.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b05305.

Two tables listing computed coordinates and enthalpies of species and transition states considered in the mechanisms for C_2F_4 , CFCICFCl , and C_4F_6 (PDF)

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Notes

The authors declare no competing financial interest.

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