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# Rate coefficients for the chemical reactions of $\text{CH}_2\text{F}_2$ , $\text{CHClF}_2$ , $\text{CH}_2\text{FCF}_3$ and $\text{CH}_3\text{CCl}_3$ with $\text{O}(^1\text{D})$ at 298 K

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## Chemical Physics Letters

journal homepage: [www.elsevier.com/locate/cplett](http://www.elsevier.com/locate/cplett)Rate coefficients for the chemical reactions of CH<sub>2</sub>F<sub>2</sub>, CHClF<sub>2</sub>, CH<sub>2</sub>FCF<sub>3</sub> and CH<sub>3</sub>CCl<sub>3</sub> with O(<sup>1</sup>D) at 298 KE.J.K. Nilsson<sup>a,\*</sup>, V.F. Andersen<sup>b</sup>, O.J. Nielsen<sup>b</sup>, M.S. Johnson<sup>b,\*</sup><sup>a</sup> Division of Combustion Physics, Department of Physics, Lund University, Professorgatan 1, SE-223 63 Lund, Sweden<sup>b</sup> Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

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## ABSTRACT

The rate coefficients for the chemical reactions (species loss rates, quenching excluded) of the refrigerants CH<sub>2</sub>F<sub>2</sub> (HFC-32), CHClF<sub>2</sub> (HFC-22) and CH<sub>2</sub>FCF<sub>3</sub> (HFC-134a), and the solvent CH<sub>3</sub>CCl<sub>3</sub> with O(<sup>1</sup>D) are determined relative to CH<sub>4</sub> + O(<sup>1</sup>D) at 298 K. The resulting rates  $k(\text{CH}_2\text{F}_2 + \text{O}(\text{}^1\text{D})) = (4.78 \pm 1.03) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k(\text{CHClF}_2 + \text{O}(\text{}^1\text{D})) = (8.69 \pm 1.72) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k(\text{CH}_2\text{FCF}_3 + \text{O}(\text{}^1\text{D})) = (6.10 \pm 1.43) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  are compared to available literature data. The reaction rate of 1,1,1-trichloroethane with O(<sup>1</sup>D) is determined for the first time,  $k(\text{CH}_3\text{CCl}_3 + \text{O}(\text{}^1\text{D})) = (2.93 \pm 1.20) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

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## 1. Introduction

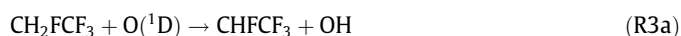
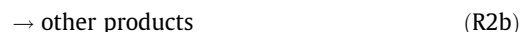
The <sup>1</sup>D excited state of the oxygen atom plays a special role in atmospheric chemistry. Its unusual reactivity arises from a potential energy 189.8 kJ mol<sup>-1</sup> above the <sup>3</sup>P ground state [1]. The photolysis of ozone at  $\lambda < 328 \text{ nm}$  produces O(<sup>1</sup>D) with a quantum yield of 0.90 at  $\lambda < 306 \text{ nm}$ . Most atmospheric O(<sup>1</sup>D) is collisionally quenched but a fraction reacts with H<sub>2</sub>O to produce two hydroxyl radicals, the main atmospheric oxidant [2,3]. However, under the bright, high ozone, low pressure and dry conditions of the upper stratosphere, O(<sup>1</sup>D) itself becomes an important oxidant towards many atmospheric trace gases, including the HFCs, N<sub>2</sub>O and methane, with [O(<sup>1</sup>D)] ranging from less than 0.1 cm<sup>-3</sup> at the surface to more than 100 cm<sup>-3</sup> in the upper stratosphere [4]. According to modeling by McCarthy et al. [5] 10–30% of stratospheric methane is removed by reaction with O(<sup>1</sup>D). Despite their importance, O(<sup>1</sup>D) reactions have not been studied as extensively as Cl and OH reactions. The lack of O(<sup>1</sup>D) data is likely due to experimental difficulties, e.g. generating and detecting O(<sup>1</sup>D), and interference from OH reactions.

CH<sub>2</sub>F<sub>2</sub>, CHClF<sub>2</sub> and CH<sub>2</sub>FCF<sub>3</sub> are used as refrigerants and are potent greenhouse gases when emitted into the atmosphere; CHClF<sub>2</sub> and CH<sub>2</sub>FCF<sub>3</sub> are ozone depleting substances and CHClF<sub>2</sub> is regulated by the Montreal Protocol on Substances that Deplete the Ozone Layer [6,7].

1,1,1-trichloroethane, CH<sub>3</sub>CCl<sub>3</sub>, was widely used as an industrial solvent until restricted by the Montreal Protocol. Arguably the best estimates of the global average OH concentration are based on

applying mass balance to CH<sub>3</sub>CCl<sub>3</sub>, using production statistics, its atmospheric concentration, and rates of in situ removal e.g. OH reaction and photolysis [3,8,9]. It is therefore important to quantify the CH<sub>3</sub>CCl<sub>3</sub> reaction rate with O(<sup>1</sup>D). In the stratosphere OH contributes 40–80% of oxidative removal, with O(<sup>1</sup>D) and Cl also playing significant roles [5]. Partitioning between the removal processes varies with altitude, latitude and time of year.

In the present Letter the reactive loss channels of the title compounds in R1, R2, R3, and R4 below were determined relative to the rate of Reaction 5. The experiments were simulated using a chemical kinetics model, to take into account possible interference by OH reactions.



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The product channels listed here include abstraction but not quenching as it does not remove reagents, the observables in the experiments and the atmosphere. The main reaction in R1–R5 is hydrogen abstraction. The products of hydrogen abstraction are OH and a radical that may undergo further reaction. Halogen atom abstraction is also possible as occurs e.g. in Reaction 2, where the chlorine is abstracted to yield ClO [10]; ClO does not react with CH, CF or CCl bonds under these conditions. Previous relative and absolute rate studies of R1–R3 are summarized in Table 1. The reaction of trichloroethane with O(<sup>1</sup>D), R4, has not been investigated previously. The rate given in the most recent JPL data evaluation was used for R5 [11]. The first column of Table 1 presents the overall rates of the reactions,  $k_{\text{total}}$ , i.e. loss of O(<sup>1</sup>D). The second column shows the quenching branching ratio, resulting in no loss of the reagent molecule but deactivation of oxygen. Next the loss of reactants is presented as a range of values including all sources of error, e.g. experimental errors in determinations of overall rates, uncertainties in branching ratios and errors in reference reactions used in relative rate studies.

Reaction 1, CH<sub>2</sub>F<sub>2</sub> + O(<sup>1</sup>D), has previously been investigated in a relative rate study where N<sub>2</sub>O + O(<sup>1</sup>D) was used as the reference reaction [12], and in an absolute rate study [13]. In the relative rate study the loss of CH<sub>2</sub>F<sub>2</sub> was monitored, and thus  $k_{\text{R1a}}$  was directly determined. The rate relative to  $k_{\text{N}_2\text{O}+\text{O}(\text{1D})}$  was determined to be  $0.4 \pm 0.2$ , which gives an absolute rate of  $k_{\text{R1a}} = (5.08 \pm 2.54) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , using the currently recommended value for the reference reaction [11]. The absolute rate study [13] yielded a reaction rate coefficient for the overall reaction  $k_{\text{R1a}} + k_{\text{R1b}}$  and a value for the branching into the quenching channel  $k_{\text{R1b}}/(k_{\text{R1a}} + k_{\text{R1b}})$ , determined from the experimental yield of O(<sup>3</sup>P). These values are presented in Table 1, and used to calculate the reaction rate coefficient for reaction into the product channel,  $k_{\text{R1a}}$ , presented as a range in column 3. With uncertainties in both  $k_{\text{R1b}}$  and the branching ratio, determinations of  $k_{\text{R1a}}$  span a range of about a factor of 5. The value for the overall reaction rate given by Schmoltner et al. is similar to the value given by Green and Wayne for the product channel, but due to the large uncertainties the upper limit calculated from the Schmoltner et al. data is close to the lower limit of the Green and Wayne data [12,13]. The JPL [11] and IUPAC [14] data compilations use the result of Schmoltner et al. as their recommendation for the overall rate. IUPAC recom-

mends the branching ratio from that study, with increased uncertainties.

The overall reaction of CHClF<sub>2</sub> with O(<sup>1</sup>D),  $k_{\text{R2a}} + k_{\text{R2b}} + k_{\text{R2c}}$ , has been determined in two absolute rate studies with good agreement [15,16]; Warren et al. also determined the branching ratio into the quenching channel,  $k_{\text{R2c}}$ . In the relative rate study by Green and Wayne [12] discussed above for CH<sub>2</sub>F<sub>2</sub>,  $k_{\text{R2a}} + k_{\text{R2b}}$  was determined to be  $0.8 \pm 0.2$  relative to  $k_{\text{N}_2\text{O}+\text{O}(\text{1D})}$ . As seen in the third column of Table 1 this result has a significant overlap with the range determined from the results of Warren et al. A relative rate study by Atkinson et al. [10], gives a result that is twice as high.

For Reaction 3 the two available absolute rate studies, by Warren et al. [15] and by Kono and Matsumi [17], show excellent agreement in the overall rate,  $k_{\text{R3a}} + k_{\text{R3b}} + k_{\text{R3c}}$ , but large divergence in the branching into the quenching channel,  $k_{\text{R3c}}/(k_{\text{R3a}} + k_{\text{R3b}} + k_{\text{R3c}})$ , with the results of Warren et al. [15] implying that this could possibly be the only important channel. This results in a wide range for the predicted rate into product channels,  $k_{\text{R3a}} + k_{\text{R3b}}$ . The JPL data evaluation recommends the product yields of Kono and Matsumi since C–H bonds usually are reactive towards O(<sup>1</sup>D), while the IUPAC data evaluation chose to recommend a value with large uncertainties covering the ranges of both studies [11,14].

From Table 1 and the discussion above it is seen that previous results are inconsistent concerning the rate of removal of the halocarbons for all of these reactions. In most studies the halocarbon removal was determined indirectly from the loss of O(<sup>1</sup>D) and/or production of O(<sup>3</sup>P). In this Letter we use the relative rate method with direct observation of species concentrations. Some hydroxyl is unavoidably produced in the experiments, so a photochemical model is used to estimate this small loss and correct the result. The rate constant of the reference reaction has been determined in three studies with good agreement; we refer to the JPL data compilation [11] and the IUPAC data sheet [14].

## 2. Experimental

### 2.1. Photochemical reactor

The photochemical reactor at the Copenhagen Center for Atmospheric Research consists of a temperature controlled 100 L quartz cylinder with multipass optics, described elsewhere [18]. Experi-

**Table 1**  
Summary of available literature data, from experimental studies and data compilations, for reaction of CH<sub>2</sub>F<sub>2</sub>, CHClF<sub>2</sub> and CH<sub>2</sub>FCF<sub>3</sub> with O(<sup>1</sup>D).

$k_{\text{total}}/10^{-11} \text{ molecule cm}^{-3} \text{ s}^{-1}$	$k_{\text{quenching}}/k_{\text{total}}$	$k_{\text{HFC}+\text{O}(\text{1D})\rightarrow\text{products}}/10^{-11} \text{ molecule cm}^{-3} \text{ s}^{-1}$	Method	Reference
CH <sub>2</sub> F <sub>2</sub> (HFC-32)				
		2.54–7.62	Relative rate, $k_{\text{N}_2\text{O}+\text{O}(\text{1D})}$ <sup>a</sup>	[12]
5.13 ± 0.33	0.70 ± 0.11	0.64–2.43	VUV atomic resonance fluorescence O( <sup>3</sup> P) detection	[13]
5.1 ± 0.3	0.7 ± 0.2	0.51–2.55	IUPAC data evaluation	[14]
5.1 ± 1.0			JPL data evaluation	[11]
		4.78 ± 1.03		This Letter
CHClF <sub>2</sub> (HCFC-22)				
		7.62–12.7	Relative rate, $k_{\text{N}_2\text{O}+\text{O}(\text{1D})}$ <sup>a</sup>	[12]
		17.8–22.9	Relative rate, $k_{\text{N}_2\text{O}+\text{O}(\text{1D})}$ <sup>a</sup>	[10]
9.5 ± 3.0			O( <sup>1</sup> D) detection by Vis–UV emission	[16]
10.8 ± 2.0	0.28 ± 0.06	5.8–10.0	VUV atomic resonance fluorescence O( <sup>3</sup> P) detection	[15]
10.0 ± 1.0	0.28 ± 0.1	5.58–9.02	IUPAC data evaluation	[14]
10.0 ± 1.5			JPL data evaluation	[11]
		8.69 ± 1.72		This Letter
CH <sub>2</sub> FCF <sub>3</sub> (HFC-134a)				
4.85 ± 0.25	0.94 (+0.06/–0.1)	0.0–4.28	VUV atomic resonance fluorescence O( <sup>3</sup> P) detection	[15]
4.9 ± 0.5	0.65 ± 0.06	1.28–2.21	LIF, O( <sup>1</sup> D) detection	[17]
4.9 ± 0.1	0.80 ± 0.15	0.25–1.72	IUPAC data evaluation	[14]
4.9 ± 0.75	<sup>b</sup>		JPL data evaluation	[11]
		6.10 ± 1.43		This Letter

<sup>a</sup> Recalculated using the currently recommended value of the rate of the reference reaction,  $k_{\text{N}_2\text{O}+\text{O}(\text{1D})} = 1.27 \times 10^{-10} \text{ molecule cm}^{-3} \text{ s}^{-1}$ , from JPL [11].

<sup>b</sup> Product yields by Kono and Matsumi [17] are recommended by JPL [11].

ments were performed by exposing mixtures of reactants, reference compound ( $\text{CH}_4$ ) and ozone to UVC light with a strong emission at 254 nm to produce  $\text{O}(^1\text{D})$  via R6. The reaction mixture was monitored using a Bruker 66v/S FTIR spectrometer. Ozone was generated from  $\text{O}_2$  using an ozone generator (Model AC-20, O3 Technology) and preconcentrated on silica gel cooled with ethanol and dry ice at ca.  $-67^\circ\text{C}$ .



There is a competition for  $\text{O}(^1\text{D})$ , between chemical Reactions R1–R5 and R7, and quenching, R8.



R7 (and R8) is considered below in the model, as hydroxyl also removes the target compounds, the amount depending on the rate constants of the reactions and the radical concentrations. Hydroxyl rate constants for the title compound are on the order of  $10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ , while  $\text{O}(^1\text{D})$  rate constants are about  $10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ . Therefore,  $[\text{OH}]$  could be several orders of magnitude larger than  $[\text{O}(^1\text{D})]$  before significantly affecting reagent concentrations.

Methane,  $\text{CH}_4$ , is chosen as the reference compound for two reasons; it has well established rate coefficients with  $\text{O}(^1\text{D})$  and OH, and there is a significant difference in its reactivity towards the two radicals.

Quenching, R8, is minimized by keeping the system pressure low. Experiments were performed with  $\text{N}_2$  bath gas at 50 mbar, or without bath gas, giving a total pressure below 2 mbar. Production of hydroxyl was minimized by keeping  $[\text{H}_2\text{O}]$  to a minimum. Before experiments the chamber was heated to  $35^\circ\text{C}$  and pumped to drive out water.

Experiments were performed at  $298.0 \pm 0.5 \text{ K}$ . Gas mixtures were typically photolyzed in 6–15 steps of 10–30 s. An FTIR spectrum consisting of 32 coadded interferograms recorded at a resolution of  $0.125 \text{ cm}^{-1}$  was obtained after each step. The mixtures were allowed to stabilize for 2 min after each photolysis step before recording an IR spectrum. Table S1 (Supplementary Information) lists the composition of reaction mixtures including total pressure, and the spectral region used to determine concentrations. Figures 1 and 2 show the loss of reagents with time in typical experiments.

Control experiments checked for dark loss of reactants and reference compound. There was no significant loss when mixtures

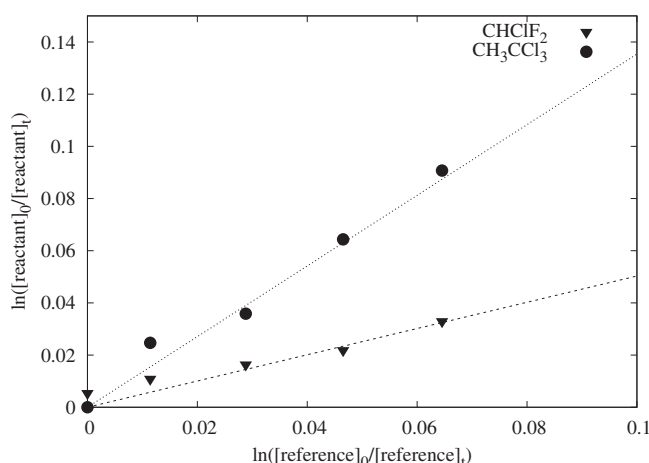


Figure 1. Plot of rates of loss of  $\text{CH}_3\text{CCl}_3$  and  $\text{CHClF}_2$  relative to that of  $\text{CH}_4$ .

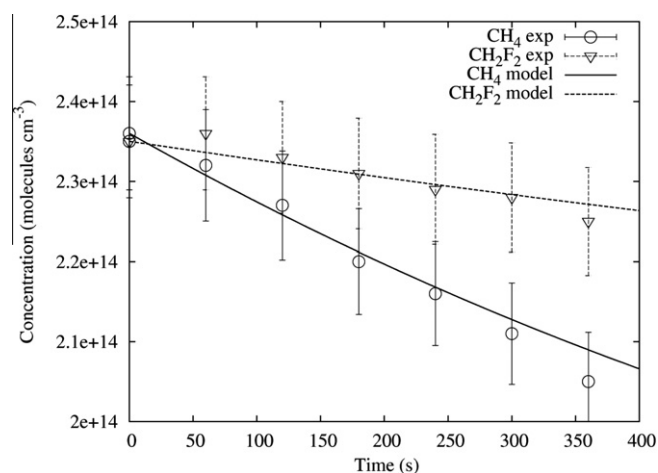


Figure 2. Concentrations of the reactant  $\text{CH}_2\text{F}_2$  and the reference compound  $\text{CH}_4$ , as a function of time, in experiment 1, the symbols represent experimental data and the lines are results of a model simulation.

were left to stand in the dark for 30 min, the duration of a typical experiment. In addition, no loss was seen when the gases were irradiated in the absence of  $\text{O}_3$ .

## 2.2. Data analysis

The spectra were analyzed using an iterative nonlinear least squares fitting procedure [19]. Reference spectra of  $\text{CH}_4$ ,  $\text{O}_3$  and  $\text{H}_2\text{O}$  were taken from the HITRAN database [20]. Spectra were analyzed for  $\text{CH}_4$  in the region  $2800\text{--}3200 \text{ cm}^{-1}$ . Reference spectra of  $\text{CH}_2\text{F}_2$ ,  $\text{CHClF}_2$ , and  $\text{CH}_2\text{FCF}_3$  and  $\text{CH}_3\text{CCl}_3$  were recorded under the same conditions as for the photolysis experiments. These spectra are available in the EUROCHAMP FTIR Reference Spectra Database [21]. Spectra from the relative rate experiments were analyzed in the regions  $1400\text{--}1480 \text{ cm}^{-1}$  for  $\text{CH}_2\text{F}_2$ ,  $1310\text{--}1580 \text{ cm}^{-1}$  for  $\text{CHClF}_2$ ,  $3500\text{--}3900$  or  $1310\text{--}1580 \text{ cm}^{-1}$  for  $\text{CH}_2\text{FCF}_3$ , and  $1310\text{--}1580 \text{ cm}^{-1}$  for  $\text{CH}_3\text{CCl}_3$ .

The relative rate method is an established method for measuring reaction rates, based on monitoring the loss of the reactant and the reference compound.  $\ln([\text{reactant}]_{t0}/[\text{reactant}]_t)$  versus  $\ln([\text{reference}]_{t0}/[\text{reference}]_t)$  was plotted using the expression:

$$\ln\left(\frac{[\text{reactant}]_{t0}}{[\text{reactant}]_t}\right) = \frac{k_{\text{ref}}}{k_{\text{react}}} \ln\left(\frac{[\text{reference}]_{t0}}{[\text{reference}]_t}\right) \quad (1)$$

Where  $[\text{reactant}]_{t0}$ ,  $[\text{reactant}]_t$ ,  $[\text{reference}]_{t0}$  and  $[\text{reference}]_t$  are the concentrations of reactant and reference at times  $t_0$  and  $t$ , and  $k_{\text{react}}$  and  $k_{\text{ref}}$  are the rate constants for reactions with  $\text{O}(^1\text{D})$ . Plots of  $\ln([\text{reactant}]_{t0}/[\text{reactant}]_t)$  versus  $\ln([\text{reference}]_{t0}/[\text{reference}]_t)$  should be linear, pass through the origin and have a slope of  $k_{\text{react}}/k_{\text{ref}}$ ; fits were not forced to pass through the origin. Figure 1 shows typical relative rate plots from experiments 4 and 5, which is one single experiment including both  $\text{CHClF}_2$  and  $\text{CH}_3\text{CCl}_3$ .

The relative rate method is used when the studied reaction is the only significant loss process for the reactant. Here there is a complication due to possible competition from OH. Similar circumstances have been encountered in other relative rate studies of  $\text{O}(^1\text{D})$  reactions [22], as well as photolysis rate studies [23]. In these cases models were used to better quantify the chemical systems. Nilsson et al. [23] estimated  $[\text{OH}]$  and used it to correct the relative rates. Similarly, Saueressig et al. [22] estimated the relative rate (RR) for an  $\text{O}(^1\text{D})$  reaction using the relation:  $\text{RR}_{\text{meas}} = c \times \text{RR}_{\text{OH}} + (1 - c) \times \text{RR}_{\text{O}(^1\text{D})}$ . Here  $\text{RR}_{\text{meas}}$  is known from the experiment,  $\text{RR}_{\text{OH}}$  (the relative rate for the OH reaction) is



known from the literature, and  $c$  is the fraction of reactant lost to OH reaction, estimated from the model.

For the present Letter reaction rates with hydroxyl are known so the relative rates  $RR_{OH}$  can be determined. The final result is affected by errors in the OH reaction rates. As mentioned  $RR_{meas}$  is known from the experiments. The values of  $RR_{OH}$  calculated from the JPL and IUPAC evaluations the OH reactions are 1.75, 0.73, 0.66 and 1.52 for  $CH_2F_2$ ,  $CHClF_2$ ,  $CH_2FCF_3$  and  $CH_3CCl_3$  respectively. As each experiment has a unique set of conditions, interference from OH will vary, and therefore it must be evaluated separately for each experiment. Initial simulations are performed using estimated values of  $k_{1a}$ ,  $k_{2a} + k_{2b}$ ,  $k_{3a} + k_{3b}$  and  $k_4$ , based on previous determinations or the reactivity of similar compounds. This procedure is repeated for each experiment for a certain compound. The rate constants are modified until the simulations correctly model the loss of reactant concentrations and the same relative rates,  $RR_{meas}$ , as determined from experiments.

### 3. Chemical kinetics model

The goal of the model is to evaluate the role of OH reactions and use this information to correct the  $O(^1D)$  rate results. An initial model with 105 reactions was built using Kintecus [24] and rates from evaluations [10,11] and the literature [16,25–28]. The reactions were evaluated to remove unnecessary reactions yielding a final model with 34 reactions involving  $O_x$  and  $HO_x$ , and the oxidation of methane, see Table S2 (Supplementary Information). The full model including the title compounds, is available as Electronic Supplementary Information. Sources of water must be taken into account, as well as other processes forming OH. Input parameters include the initial concentrations of methane, halocarbon, ozone and water, for each experiment, determined by spectral fitting. Figure 2 shows the concentrations of  $CH_2F_2$  and  $CH_4$  with time as an example of modeled and experimental concentrations.

It is essential that the model makes a good estimate of OH concentrations. Sensitivity analysis shows that OH is sensitive to reactions (with the most sensitive listed first) 1, 16, 13, 14, 5, 6, 7, 17 and 21 in Table S2 (Supplementary Information).

Table 2 shows the relative rates  $RR_{meas}$  derived from experiments, with no adjustment for OH reactions. The second column shows  $k_{O(^1D)}$  obtained from experiment. The total loss towards  $O(^1D)$  is shown in the third column, derived from the model; the remainder is lost via OH. The fraction lost via  $O(^1D)$  varies significantly and depends on the reaction rates towards OH and  $O(^1D)$  and on the production of OH, mainly due to  $[H_2O]$ . The water concentration was varied to quantify the sensitivity for two experiments selected to span the range of conditions: experiment 1 in which >50% of the test compound was lost to OH, and experiment 3 in which ~15% was lost to OH. These experiments were not significantly sensitive to the initial water concentration: when the

initial water concentration was decreased by a factor of 10 the loss via OH decreased by 2.2% for experiment 1, and 0.5% for experiment 3. However, the sensitivity was larger towards an increase in water; for experiment 1 doubling water changed the partitioning between reaction with  $O(^1D)$  and OH by a few percent, while for experiment 3 a change of a factor of 10 was required to significantly affect the results. As the error in determining  $[H_2O]$  in the experiments is <5% we conclude that the most important source of OH is sufficiently quantified. The model shows that the most important source of water in the experiment is in situ chemistry and not the (variable) background concentration in the reactor.

Figures S1 and S2 (Supplementary Information) show examples of  $[CH_2FCF_3]$ ,  $[CH_4]$  and  $[H_2O]$  for experiments at different total pressures. In both cases there is agreement between experiment and model for  $[CH_4]$  and  $[CH_2FCF_3]$ .

### 4. Results and discussion

Here we present and discuss the results in relation to earlier work. Each reaction rate constant is determined in several experiments and the final values are the averages of two to four independent experiments. The error bars include uncertainty in the slope of the relative rate plots, uncertainty in the rate constant of the reference reaction, and an additional 5% error to take into account possible errors in the model simulations.

#### 4.1. $CH_2F_2 + O(^1D) \rightarrow$ products

The results of two experiments are presented in Table 2 (experiments 1 and 2), and available literature values in Table 1. The final value is  $k_{CH_2F_2+O(^1D)\rightarrow products} = (4.78 \pm 1.03) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The value recommended by IUPAC is the result by Schmoltner et al. [13], an absolute rate study where only  $O(^3P)$  was monitored and other quantities were determined indirectly. Green and Wayne [12] used the relative rate method and followed the loss of halocarbons using IR spectroscopy, and considering the large error bars in their result it is in agreement with the result of the present Letter. The new result is close to the lowest value in the range by Green and Wayne, and at the higher end of the range by Schmoltner et al. Reactive loss is important for these compounds, and the result of the present Letter reduces the uncertainty for this particular reaction, yielding a value at the higher end of the interval recommended by IUPAC [14].

#### 4.2. $CHClF_2 + O(^1D) \rightarrow$ products

The result is based on two experiments with an average value of  $(8.69 \pm 1.72) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Experiment 4 was performed at a pressure of only a few mbar, while experiment 3 was at 20 mbar; no difference due to pressure is seen.

**Table 2**  
Experimental relative rates, final rate coefficients for the individual experiments (derived using chemical kinetics modeling), and the amount of reactant lost to the title reactions. Errors in relative rates is the uncertainty of the slope in equation 1. Errors in  $k_{O(^1D)}$  include also 5% error for possible uncertainties in model simulations, and uncertainty of the rate coefficient of the reference reaction.

	Exp.	$RR_{meas}$	$k_{O(^1D)}/(\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1})$	Loss to $O(^1D)$ reaction/%
$CH_2F_2$	1	$0.264 \pm 0.027$	$(4.6 \pm 0.9) \times 10^{-11}$	44
	2	$0.282 \pm 0.019$	$(4.9 \pm 0.8) \times 10^{-11}$	48
$CHClF_2$	3	$0.490 \pm 0.016$	$(8.6 \pm 1.4) \times 10^{-11}$	84
	4	$0.503 \pm 0.046$	$(8.8 \pm 1.6) \times 10^{-11}$	84
$CH_3CCl_3$	5	$1.354 \pm 0.098$	$(2.4 \pm 0.4) \times 10^{-10}$	86
	6	$1.994 \pm 0.190$	$(3.5 \pm 0.6) \times 10^{-10}$	91
$CH_2FCF_3$	7	$0.332 \pm 0.010$	$(5.8 \pm 0.9) \times 10^{-11}$	57
	8	$0.325 \pm 0.006$	$(5.7 \pm 0.9) \times 10^{-11}$	55
	9	$0.369 \pm 0.008$	$(6.5 \pm 1.0) \times 10^{-11}$	75
	10	$0.368 \pm 0.022$	$(6.4 \pm 1.1) \times 10^{-11}$	81

The overall rate has been determined previously with very good agreement [15,16], as reported in Table 1. Partitioning into the product channel has been determined several times [10,12,15]; results span a wide range. The IUPAC recommended value is an average of the data by Green and Wayne, and Warren et al. [14], and the results of the present Letter is within this range.

#### 4.3. $\text{CH}_2\text{FCF}_3 + \text{O}(^1\text{D}) \rightarrow \text{products}$

The rate of this reaction was determined four times, twice at 50 mbar, experiments 7 and 8, and twice at a few mbar, experiments 9 and 10. A weighted mean gives  $(6.10 \pm 1.43) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . For all four experiments the model does an excellent job of reproducing decay of reactants and production of water. As an example of this Figures S1 and S2 show the changes in  $\text{CH}_4$ ,  $\text{CH}_2\text{FCF}_3$  and water concentrations for experiments 7 (50 mbar) and 9 (1 mbar).

The rate constant for  $\text{CH}_2\text{FCF}_3 + \text{O}(^1\text{D})$  determined in the present Letter is significantly larger than that determined in previous studies, in fact it is close to the overall reaction rate,  $k_{\text{total}}$ , determined by Warren et al. [15] and Kono and Matsumi [17]. This implies that their quenching rate is severely overestimated. Both studies are absolute rate studies determining the overall rate of the reaction,  $k_{\text{total}}$ , based on measurements of  $\text{O}(^3\text{P})$  profiles; Kono and Matsumi also determined the  $\text{O}(^1\text{D})$  and OH profiles. The IUPAC recommendation is an average of two available studies that have relatively large errors [14]. The present Letter is the first in which the loss of  $\text{CH}_2\text{FCF}_3$  is used to determine the rate of reaction and the results show that the rate  $k_{\text{HFC}+\text{O}(^1\text{D})\rightarrow\text{products}}$  is close to the literature value for  $k_{\text{total}}$ .

The present Letter shows that chemical reaction accounts for over 90 % of the total reaction. Experimental data for most  $\text{O}(^1\text{D})$  reactions are rare, and the reaction rates and branching ratios recommended by data compilations are commonly based on one or a few experiments. The ratio between the quenching channel and reactant removal is highly variable for  $\text{O}(^1\text{D})+\text{CFC}$  reactions, for example quenching is 18% of the total reaction for  $\text{CH}_3\text{F}$  and 90% of the total reaction for  $\text{CHF}_3$  [14]. For the HCFCs the quenching fraction is never above one third, for example  $\text{CH}_2\text{ClCF}_3$  (20%) and  $\text{CH}_3\text{CF}_2\text{Cl}$  (26%). For the fluoromethanes the quenching fraction increases with fluorination which is also the overall trend for the fluoroethanes. However if the previous indirect studies are to be believed  $\text{CH}_2\text{FCF}_3$  is an exception to this trend with an anomalously high quenching fraction of 94%, higher even than  $\text{CHF}_2\text{CF}_3$  (85%). We argue that the 94% value is much too high, given (i) the much lower values found in the hydro-fluoro-chloro ethanes, (ii) the trend in quenching fraction in the HFCs, (iii) the uncertainty and difficulty of indirect experiments measuring  $\text{O}(^1\text{D})$  and  $\text{O}(^3\text{P})$ , and (iv) our own experimental results for the chemical abstraction rate. In addition to direct relative rate studies, we have performed two sets of intercomparison experiments using multiple samples. The first used  $\text{CHClF}_2$ ,  $\text{CH}_3\text{CCl}_3$  and  $\text{CH}_4$ . The second used  $\text{CH}_2\text{FCF}_3$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CHClF}_2$  and  $\text{CH}_4$ . These two sets of experiments on simultaneous samples yielded chemical reaction rates for  $\text{CHClF}_2$  and  $\text{CH}_2\text{F}_2$  in agreement with the literature values. We therefore argue that the chemical reaction rate obtained for  $\text{CH}_2\text{FCF}_3$  (and  $\text{CH}_3\text{CCl}_3$ ), present in the same mixture, analyzed in the same way and modeled simultaneously, is robust.

#### 4.4. $\text{CH}_3\text{CCl}_3 + \text{O}(^1\text{D}) \rightarrow \text{products}$

To the best of our knowledge this is the first determination of the rate of the reaction  $\text{CH}_3\text{CCl}_3 + \text{O}(^1\text{D})$ . Our final value  $k(\text{CH}_3\text{CCl}_3 + \text{O}(^1\text{D})) = (2.93 \pm 1.20) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is the average of two determinations. It can be compared to the reactivity of  $\text{O}(^1\text{D})$  towards similar two-carbon halogenated compounds,

$\text{CH}_3\text{CCl}_2\text{F}$ ,  $\text{CH}_3\text{CClF}_2$ ,  $\text{CH}_3\text{CF}_3$ , and  $\text{CH}_3\text{CHF}_2$ , that have rate constants in the range of  $0.5 \times 10^{-10}$ – $2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [14].

### 5. Summary and conclusions

Reaction rates have been determined for the loss of four halogenated hydrocarbons via  $\text{O}(^1\text{D})$  reaction. Studies of these reactions are scarce and in some cases contradictory. In general there is good agreement concerning the overall rate of reaction i.e. including the  $\text{O}(^1\text{D})$  quenching channel where the halogenated hydrocarbons themselves are not consumed, however, the chemical reaction channel is the most important for atmospheric applications.

Of R1–R4,  $\text{CHClF}_2 + \text{O}(^1\text{D})$  is the only in which two previous studies of loss of the reactant to excited oxygen show good agreement [12,15]. For this reaction the present result significantly reduces the uncertainty and is in excellent agreement with previous studies and the evaluation by IUPAC [14].

The IUPAC recommendation [14] for the rate of  $\text{CH}_2\text{F}_2 + \text{O}(^1\text{D})$  is based on one previous study [13], while an older study reports a faster rate with large error bars. The result reported in the present Letter is slightly higher than the result of Schmoltner et al. but well within the error bars, and reduces the uncertainty.

Previous studies of  $\text{CH}_2\text{FCF}_3$  conclude that a large part of the reaction with  $\text{O}(^1\text{D})$  is quenching, not reaction, based on two studies with relatively uncertain results for the product channels [15,17]. The present Letter contradicts the earlier work; the rate into product channels determined here is close to the overall reaction rate determined in absolute rate studies. This implies that reaction rather than quenching is the most important process, in agreement with the trend for similar compounds.

The rate of the reaction  $\text{CH}_3\text{CCl}_3 + \text{O}(^1\text{D})$  has been determined for the first time. This rate is important for understanding the stratospheric chemistry of trichloroethane (methyl chloroform), since the relatively fast reaction rate implies that reaction with excited oxygen is an important removal process for  $\text{CH}_3\text{CCl}_3$  in the stratosphere. A simple estimate based on concentrations and actinic flux in DeMore et al. [4] shows that  $\text{O}(^1\text{D})$  reaction will be a significant loss process for  $\text{CH}_3\text{CCl}_3$  in the tropopause and lower stratosphere, although slower than photolysis or OH reaction. We anticipate that the result of this Letter will be used in future models of the atmospheric chemistry of the four title compounds.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2012.10.001>.

### References

- [1] C.E. Moore Tables of Spectra of Hydrogen, Carbon, Nitrogen, and Oxygen 1993, CRC Press, Boca Raton, 1993.
- [2] H. Levy Science 173 1971 141.
- [3] S.A. Montzka, M. Krol, E. Dlugokencky, B. Hall, P. Jockel, J. Lelieveld Science 331 2011.
- [4] W.B. DeMore et al. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling Evaluation Number 12 1997, National Aeronautics and Space Administration, 1997.
- [5] M.C. McCarthy, K.A. Boering, A.L. Rice, S.C. Tyler, P. Connell, E. Atlas. Geophys. Res., [Atmos.] 108 2003.
- [6] T.J. Wallington, W.F. Schneider, D.R. Worsnop, O.J. Nielsen, J. Sehested, W.J. Debruyne, J.A. Shorter Environ. Sci. Technol. 28 1994 A320.

- [7] S.D.Solomon et al.IPCC 2007: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, in: S.D.Solomon (Ed.)2007, IPCC, Cambridge, United Kingdom and New York, NY, USA, 2007.
- [8] R.G.Prinn et al.Science 2691995 187.
- [9] J.S.Wang, M.B.McElroy, J.A.Logan, P.I.Palmer, W.L.Chameides, Y.X.Wang, I.A.Megretskaja]. Geophys. Res., [Atmos.] 1132008.
- [10] R.Atkinson, G.M.Breuer, J.N.Pitts, H.L.Sandoval]. Geophys. Res. Oceans Atmos. 811976 5765.
- [11] S.P. Sander, J. Abbatt, J.R. Barker, J.B. Burkholder, R.R. Friedl, D.M. Golden, R.E. Huie, C.E. Kolb, M.J. Kurylo, G.K. Moortgat, V.L. Orkin, P.H. Wine, Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation No. 17. JPL Publication 10–6, Jet Propulsion Laboratory, Pasadena, 2011.
- [12] R.G.Green, R.P.Wayne]. Photochem. 61977 371.
- [13] A.M.Schmoltner et al.J. Phys. Chem. 971993 8976.
- [14] R.Atkinson et al.Atmos. Chem. Phys. 82008 4141.
- [15] R.Warren, T.Gierczak, A.R.Ravishankara]. Chem. Phys. Lett. 1831991 403.
- [16] J.A.Davidson, H.I.Schiff, T.J.Brown, C.J.Howard]. Chem. Phys. 691978 4277.
- [17] M.Kono, Y.Matsumij. Phys. Chem. A 1052001 65.
- [18] E.J.K.Nilsson, C.Eskebjerg, M.S.Johnson]. Atmos. Environ. 432009 3029.
- [19] D.W.T.Griffith]. Appl. Spectrosc. 501996 59.
- [20] L.S.Rothman et al.J. Quant. Spectrosc. Radiat. Transfer 1102009 533.
- [21] EUROCHAMP-2 FTIR Reference Spectra Database, <<http://eurochamp-database.es/>, 2012>.
- [22] G.Saueressig, J.N.Crowley, P.Bergamaschi, C.Bruhl, C.A.M.Brenninkmeijer, H.Fischer]. Geophys. Res. [Atmos.] 1062001 23127.
- [23] E.J.K.Nilsson, L.Bache-Andreassen, M.S.Johnson, C.J.Nielsen]. Phys. Chem. A 1132009 3498.
- [24] J.C.Ianni]. A comparison of the Bader–Deuflhard and the Cash–Karp Runge–Kutta integrators for the GRI–MECH 3.0 model based on the chemical kinetics code Kintecus2003, Elsevier Science Bv, Amsterdam, 2003.
- [25] J.C.Tully]. Chem. Phys. 621975 1893.
- [26] J.A.Davidson, H.I.Schiff, T.J.Brown, C.J.Howard]. Chem. Phys. 691978 1216.
- [27] J.Albaladejo, E.Jimenez, A.Notario, B.Cabanas, E.Martinez]. Phys. Chem. A 1062002 2512.
- [28] R.Zellner, D.Hartmann, J.Karthauser, D.Rhasa, G.Weibring]. Chem. Soc., Faraday Trans. 21988 549.