

Reaction rate constants of $\text{OH} + \text{CHF}_3 \rightarrow \text{products}$ and $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$ at 500–750 K

L.J. Medhurst^a, J. Fleming^b, H.H. Nelson^c

^a Marymount University, School of Arts and Sciences, 2807 N. Glebe Rd., Arlington VA 22207, USA

^b Chemistry Division, Code 6185, Naval Research Laboratory, Washington DC 20375-5342, USA

^c Chemistry Division, Code 6111, Naval Research Laboratory, Washington DC 20375-5342, USA

Received 14 August 1996; in final form 26 December 1996

Abstract

The reactions $\text{OH} + \text{CHF}_3 \rightarrow \text{products}$ and $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$ were studied in the temperature range 500–750 K and the pressure range 20–160 Torr using laser-induced-fluorescence detection of OH. For the reaction, $\text{OH} + \text{CHF}_3$, the experimental rate coefficient is $k = (1.1 \pm 0.3) \times 10^{-12} \exp(-(2300 \pm 200)/T)$. For the reaction $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH}$, the rate coefficient is $k = (2.49 \pm 0.06) \times 10^{-13} \exp(-(3000 \pm 1000)/T)$ in the temperature range studied. For the reaction $\text{CF}_3\text{CFHCF}_3 + \text{O}(^3\text{P}) \rightarrow \text{OH} + \text{CF}_3\text{CFCF}_3$, an upper limit for the rate coefficient is determined to be $k < (3.6 \pm 2.2) \times 10^{-13} \exp(-(2700 \pm 400)/T)$.

1. Introduction

The major fire suppression agents used in confined spaces or to protect electronics are halon 1301, CF_3Br , and halon 1211, CF_2ClBr , which are effective and relatively nontoxic. However because of their ozone depletion potential, their production is now banned under the Montreal Protocol [1]. The search for new flame suppressants which are effective, nontoxic and have low global environmental impact has sparked increased interest in the mechanisms of fire suppression and the development of predictive flame models [2–5]. Previous work has shown that the major mechanism of flame suppression by halon 1301 is catalytic removal of H atoms by Br, but that CF_3 is also capable of removing some H atoms [6,7]. Therefore, among the compounds proposed as suitable replacements for halons are hydrofluorocarbons, since they do not contribute to

ozone depletion or significantly to global warming [8] and are also known to have some fire suppression ability.

The hydrofluorocarbons, CHF_3 and CF_3CHF_2 , are currently being offered commercially as halon replacements. CHF_3 is also the smallest hydrofluorocarbon and therefore the primary model compound for mechanistic understanding and code development. The atmospheric fate of these compounds has been investigated [8]. However, very little work has been done at the higher temperatures relevant to flame chemistry. This lack of relevant kinetic data is one of the problems limiting the application of fire suppression models for hydrofluorocarbons [2]. The reaction rates of many important compounds for hydrofluorocarbon flame chemistry with the major reactive flame species: H, $\text{O}(^3\text{P})$, and OH are not well known near flame temperatures. Therefore we have undertaken a program to determine the reaction

rates of these species with the major flame radicals. As the first effort in this program, we have measured the rates of the reactions $\text{OH} + \text{CHF}_3$ and $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$ and determined an upper limit for the rate of the reaction $\text{O}(^3\text{P}) + \text{CF}_3\text{CFHCF}_3 \rightarrow \text{OH} + \text{CF}_3\text{CFCF}_3$.

2. Experimental procedure

For all the reactions studied, OH concentration was monitored either as a reactant or a product using laser pump–probe techniques. For $\text{OH} + \text{CHF}_3$, OH radical was generated by 248 nm photolysis of HNO_3 using the mildly focussed output of an excimer laser (Lambda Physik Model 201 MSC). The initial concentration of OH was calculated to be approximately $4 \times 10^{10} \text{ cm}^{-3}$, using the measured cross section [9], HNO_3 concentration and laser fluence. For the reactions in which OH was initially created by flash photolysis, the OH concentration was always observed to decrease with first-order kinetics. $\text{O}(^3\text{P})$ was generated by 193 nm photolysis of SO_2 using the same laser. The calculated initial concentration of $\text{O}(^3\text{P})$ is $4 \times 10^{14} \text{ cm}^{-3}$. For the reactions $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$ and $\text{O}(^3\text{P}) + \text{CF}_3\text{CFHCF}_3 \rightarrow \text{OH} + \text{CF}_3\text{CFCF}_3$, OH concentration was monitored and exhibited the kinetics for two first-order reactions in series.

The density of OH was measured by laser-induced-fluorescence (LIF) using the frequency doubled output of an excimer pumped dye laser (Lambda Physik Model 101 MSC/FL2002) with Coumarin 540A dye and a KDP doubling crystal (Inrad). The Q_{11} line of the $\text{A}^2\Sigma^+ - \text{X}^2\Pi$, (1, 0) band near 281.91 nm was used as the excitation for most experiments. However, other lines in this band were used with no significant difference in the observed rate constants. Fluorescence was collected perpendicular to the collinear pump and probe beams, passed through a band pass filter ($\lambda_0 = 311 \text{ nm}$, FWHM = 14 nm) and focussed onto a RCA 31000M photomultiplier tube.

The experiments were performed in a stainless-steel cross with two opposing glass arms and suprasil Brewster's windows inside a commercial convection oven. The oven has ports for the glass arms, gas inlet, and a sapphire window for optical viewing.

The gas flows were controlled with calibrated Tylan mass flow controllers or with needle valves and Tylan mass flow meters. The total pressure was determined with an MKS capacitance manometer. Argon was the buffer gas in all experiments. SO_2 (99.98% purity) and Ar (99.998% purity) were purchased commercially (Matheson and Air Products) and used without further purification. CHF_3 (99.99% purity) was supplied by DuPont and $\text{CF}_3\text{CFHCF}_3$ (research grade, 99% purity) was supplied by Great Lakes Chemical; both were used without further purification. HNO_3 was synthesized according to the method of Johnston et al. [10] The temperature of the reaction cell was determined with a chromel–alumel thermocouple (Omega K).

3. Results and discussion

Fig. 1 shows a typical experimental plot of OH concentration versus time for $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$. The OH created in this reaction reacts with CHF_3 , and therefore its concentration versus time profile shows formation followed by decay. OH concentration versus time was fit to the equation:

$$[\text{OH}] = \frac{A_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}),$$

where k_1 is the pseudo first-order reaction rate for $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$, and k_2 is the pseudo

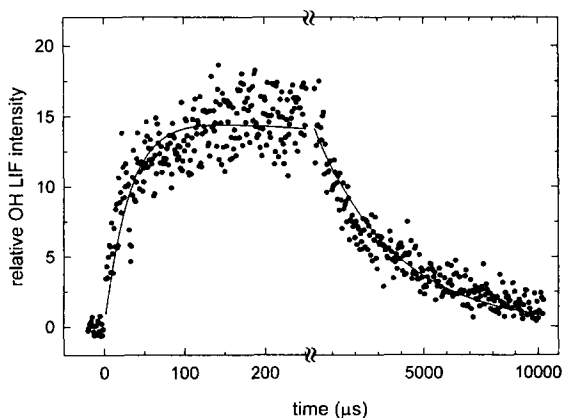


Fig. 1. Relative OH LIF intensity versus time in μs at 529 K and 28 Torr total pressure. The pressure of CHF_3 is 13.3 Torr.

first-order reaction rate for $\text{OH} + \text{CHF}_3 \rightarrow \text{products}$. A_0 , k_1 , and k_2 at each temperature and reactant concentration were determined by unconstrained three-parameter fits to $[\text{OH}]$ versus time. At each temperature the concentration of CHF_3 was varied and the slopes of k_1 and k_2 versus $[\text{CHF}_3]$ were used to determine the second-order rate coefficients for both reactions. Fig. 2 shows the plot of k_1 versus $[\text{CHF}_3]$ at 529 K. To determine if we were measuring both reactions accurately, we also measured the rate coefficient for the reaction, $\text{OH} + \text{CHF}_3 \rightarrow \text{products}$, directly by creating OH by flash photolysis of HNO_3 and observing the OH decay. These results and the results for $\text{OH} + \text{CHF}_3 \rightarrow \text{products}$ determined from the plots of k_2 versus $[\text{CHF}_3]$ described above (labeled indirect method) are summarized in Table 1 and shown with the previous results of Schmoltner et al. [11], Jeong et al. [12], Hsu and Demore [13], and the ab initio calculations of Fu et al. [14] in Fig. 3.

As can be seen from Fig. 3, the agreement of the indirect method with the direct method and the other experimental results is quite good. Also included on Fig. 3 is an Arrhenius fit to all the experimental data, the results of which are also presented in Table 4. A three-parameter fit to all the data did not improve the fit. However, this fit is also presented in Table 4.

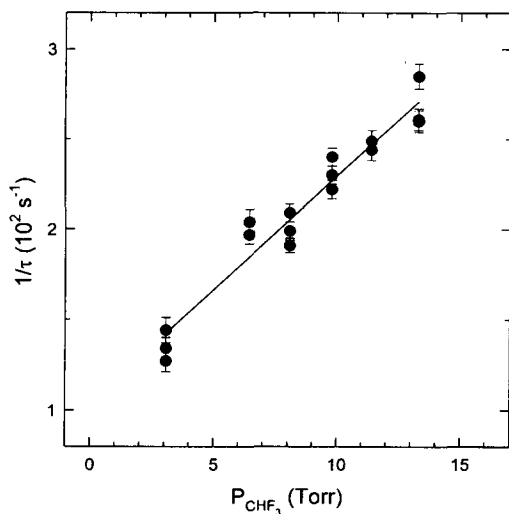


Fig. 2. Pseudo first-order rate coefficient, k_1 , in μs versus pressure of CHF_3 in Torr at 529 K. The slope of this line gives the rate coefficient for $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$.

Table 1
Measured second-order rate coefficients for $\text{OH} + \text{CHF}_3 \rightarrow \text{products}$

Temperature (K)	Pressure (Torr)	k ($10^{-15} \text{ cm}^3 \text{ s}^{-1}$) ^a
298	20	0.15 ± 0.02
351	20	1.1 ± 0.4
393	20	2.4 ± 0.2
454	20	4.1 ± 0.4
454	40	4.4 ± 0.6
454	100	5.0 ± 0.3
454	100	6.0 ± 0.2
485	20	7.2 ± 1.4
529 ^b	28	9.0 ± 2
534	20	13 ± 13
585 ^b	32	25 ± 11
594	20	24 ± 2
625 ^b	32	30 ± 4
673	20	40 ± 3
673	20	40 ± 3
673	20	37 ± 3
673 ^b	160	28 ± 4
722 ^b	160	39 ± 3
753 ^b	160	49 ± 4

^a Results are reported $\pm 2\sigma$.

^b Indirect method.

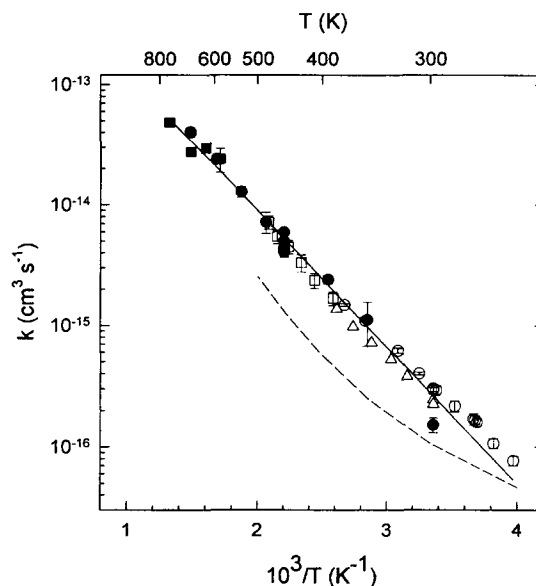


Fig. 3. Arrhenius plot for the reaction $\text{OH} + \text{CHF}_3 \rightarrow \text{products}$, k in $\text{cm}^3 \text{ s}^{-1}$ versus $1/T$ in K. (●) Experiment measured directly, (■) experiment measured from k_2 in the reaction $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$, (○) data from Ref. [11], (□) data from Ref. [12], (△) data from Ref. [13], dashed line is from Ref. [14], solid line is an Arrhenius fit to all experimental data.

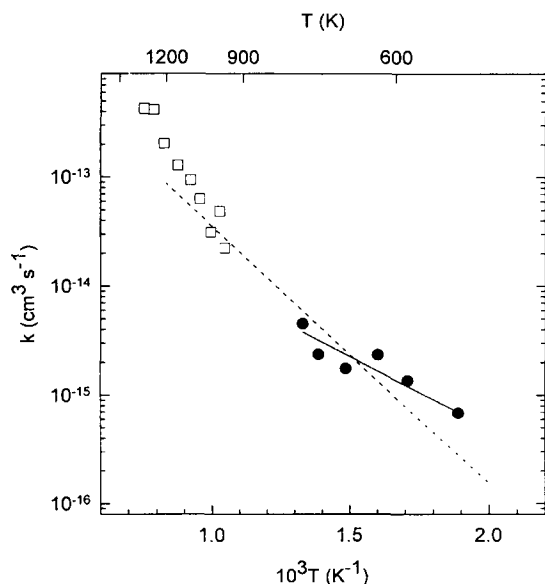


Fig. 4. Arrhenius plot for the reaction $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$, k in $\text{cm}^3 \text{s}^{-1}$ versus $1/T$ in K. (●) Experiment measured from k_1 in the reaction $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$, (□) data from Ref. [15], dashed line is from Ref. [16], solid line is an Arrhenius fit to our data.

The results for $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$ are shown in Fig. 4 with the data of Miyoshi et al. [15] and Jourdain et al. [16]. Our data are also summarized in Table 2. As can be seen from Fig. 4, our data agree reasonably well with the data of Jourdain et al., which were determined with a mass spectroscopic detection system. Unless there is extreme curvature in the reaction rate, the agreement with the results of Miyoshi et al., which was determined by a shock-tube technique, is not as good. Because the rate of this reaction is so slow and most of the expected impurities should react faster, it is difficult

Table 2

Measured second-order rate coefficients for the reaction $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$

Temperature (K)	Pressure (Torr)	k ($10^{-15} \text{ cm}^3 \text{s}^{-1}$) ^a
529	28	0.69 ± 0.09
585	32	1.4 ± 0.2
625	32	2.4 ± 0.2
673	160	1.8 ± 0.2
722	160	2.4 ± 0.3
753	160	4.5 ± 0.3

^a Results are reported $\pm 2\sigma$.

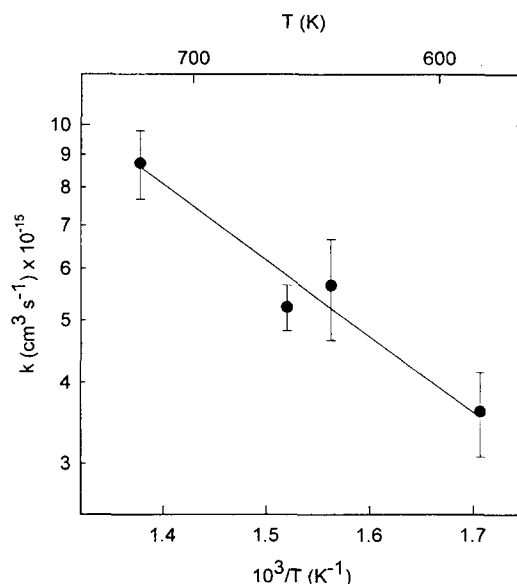


Fig. 5. Arrhenius plot for the reaction $\text{O}(^3\text{P}) + \text{CF}_3\text{CFHCF}_3 \rightarrow \text{OH} + \text{CF}_3\text{CFCF}_3$, k in $\text{cm}^3 \text{s}^{-1}$ versus $1/T$ in K. (●) Experiment measured from k_1 in the reaction $\text{O}(^3\text{P}) + \text{CF}_3\text{CFHCF}_3 \rightarrow \text{OH} + \text{CF}_3\text{CFCF}_3$, solid line is an Arrhenius fit to our data.

for anyone to report this rate with confidence. However, based on the excellent agreement of our measurements of the reaction of OH with CHF_3 , we believe we have the sample purity required to measure this rate coefficient accurately.

Our measurements for the reaction $\text{O}(^3\text{P}) + \text{CF}_3\text{CFHCF}_3 \rightarrow \text{OH} + \text{CF}_3\text{CFCF}_3$ are shown in Fig. 5 and summarized in Table 3. A comparison of direct measurements for $\text{OH} + \text{CF}_3\text{CFHCF}_3 \rightarrow$ products at temperatures near ambient with previous results [13,17] indicated that there may be some impurities in our sample that we are unable to analyze. Therefore, we are reporting the results as an upper limit. However, because of the importance of

Table 3

Measured second-order rate coefficients for the reaction $\text{O}(^3\text{P}) + \text{CF}_3\text{CFHCF}_3 \rightarrow \text{OH} + \text{CF}_3\text{CFCF}_3$

Temperature (K)	Pressure (Torr)	k ($10^{-15} \text{ cm}^3 \text{s}^{-1}$) ^a
586	40	3.7 ± 0.6
640	40	5.6 ± 1.0
658	40	5.1 ± 0.4
726	40	8.5 ± 1.2

^a Results are reported $\pm 2\sigma$.

Table 4
Temperature-dependent results

Reaction	A ($\text{cm}^3 \text{s}^{-1}$) ^a	n	E_A (K^{-1}) ^a
$\text{OH} + \text{CF}_3\text{H} \rightarrow \text{products}$ ^b	$1.1 \pm 0.3 \times 10^{-12}$		2300 ± 200
$\text{OH} + \text{CF}_3\text{H} \rightarrow \text{products}$ ^c	$1.63 \pm 0.14 \times 10^{-12}$		2600 ± 50
$\text{O}(^3\text{P}) + \text{CF}_3\text{H} \rightarrow \text{OH} + \text{CF}_3$ ^d	$2.49 \pm 0.6 \times 10^{-13}$		3000 ± 1000
$\text{O}(^3\text{P}) + \text{CF}_3\text{H} \rightarrow \text{OH} + \text{CF}_3$ ^d	$5 \pm 4 \times 10^{-18}$	1.8 ± 0.1	1900 ± 600
$\text{O}(^3\text{P}) + \text{CF}_3\text{CFHCF}_3 \rightarrow \text{OH} + \text{CF}_3\text{CFCF}_3$ ^d	$4 \pm 2 \times 10^{-13}$		2700 ± 400

^a Results are reported $\pm 2\sigma$.

^b Arrhenius fit to our direct and indirect data.

^c Arrhenius fit to data from this study, Schmoltner et al. [11], Jeong et al. [12], and Hsu et al. [13].

^d Arrhenius fit to our data only.

this reaction for flame suppression modeling, an upper limit to the rate constant is useful.

The results for the Arrhenius fits to all the temperature-dependent data are summarized in Table 4. In the case of reactions for which there are other data available in the literature, a fit to all available data is included in the table.

4. Conclusions

The reaction of $\text{O}(^3\text{P})$ with CHF_3 has a higher activation energy and a lower A -factor than the reaction of OH with CHF_3 . Therefore it seems unlikely that the reactions of $\text{O}(^3\text{P})$ with hydrofluorocarbons are important initial reactions in flames. This is especially true given that the flame zone concentration of OH is typically 5 to 10 times larger than that of $\text{O}(^3\text{P})$ [18].

Acknowledgements

This work was sponsored in part by the US Naval Sea System Command, Code 03V2. The authors thank Brad Williams for technical help. L.J. Medhurst was an ASEE summer fellow at the Naval Research Laboratory.

References

- [1] M. Freemantle, Chem. Eng. News 72 (38) (1994) 29–32.
- [2] M.R. Nyden, G.T. Linteris, D.R.F. Burgess Jr., P.R. Westmoreland, W. Tsang, M.R. Zachariah, in: Evaluation of in-flight fire suppressants for full scale testing in simulated aircraft engine nacelles and dry bays, eds. W.L. Grosshändler, R.G. Gana and W.M. Pitts (NIST SP 861, Gaithersburg, MD, 1994) pp. 467–559.
- [3] J.S. Francisco and M.M. Maricq, Adv. Photochem. 20 (1995) 79–163.
- [4] F. Battin-Leclerc, G.M. Come and F. Baronnet, Combust. Flame (1994) 644.
- [5] A.W. Miziolek and W. Tsang, eds., ACS Symposium Series 611. Halon replacements: technology and science (American Chemical Society, Washington, DC, 1995).
- [6] C.K. Westbrook, Combust. Sci. Technol. 34 (1983) 201.
- [7] R.S. Sheinson, G.I. Gellene, F.W. Williams and J.E. Hahn, Chemical and physical processes in combustion, Proceedings of Eastern Section of The Combustion Institute (1978) 18-1-18.4.
- [8] World Meteorological Organization, Atmospheric ozone, Rep. 20, Vol. II, appendix, AFEAS Rep. World Meteorol. Organ., Global Ozone Res. Monit. Proj., Geneva, 1989.
- [9] A.A. Turnipseed, G.L. Vaghjani, J.E. Thompson and A.R. Ravishankara, J. Chem Phys. 96(8) (1992) 5887.
- [10] H.S. Johnston, S.G. Chang and G. Whitten, J. Phys. Chem. 78 (1974) 1.
- [11] A.M. Schmoltner, R.K. Talukdar, R.F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S.A. McKeen and A.R. Ravishankara, J. Phys. Chem. 97 (1993) 8976.
- [12] K.M. Jeong and F. Kaufman, J. Phys. Chem. 86 (1982) 1808.
- [13] K.J. Hsu and W.B. Demore, J. Phys. Chem. 99 (1995) 1235.
- [14] Y. Fu, W. Lewis-Bevan and J. Tyrrell, J. Phys. Chem. 99 (1995) 630.
- [15] A. Miyoshi, K. Ohmori, K. Tsuchiua and H. Matsui, Chem. Phys. Lett. 204 (1993) 241.
- [16] J. Jourdain, G. LeBras and J. Combourieu, J. Chim. Phys. 75 (1978) 318.
- [17] Z. Zhang, S. Padmaja, R.D. Saini, R.E. Huie and M.J. Kurylo, J. Phys. Chem. 98 (1994) 4312.
- [18] K. Smyth and P. Tjossem, 23rd Symp. (Int.) Combust. The Combustion Institute (1990) 1829.