CHAPTER 3 – SUPPLEMENT 3

Evaluation of Atmospheric Loss Processes: Cl Kinetics Supplement

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Rate coefficients for the reaction of the Cl atom with the compounds included in the SPARC Lifetime report have received various amounts of attention. The table and figures included in this supplement contain (1) a summary of the available literature data, (2) the SPARC recommendation for the Cl reaction-rate coefficient and the basis of the recommendation, and (3) the uncertainty range in the recommended reaction-rate coefficient.

The uncertainties quoted herein follow the format given in the NASA/JPL[1] data evaluation where the uncertainty factor $f(T)$ corresponds to the 1σ estimated uncertainty in the rate coefficient, $k(T)$ at temperature T

$$f(\mathrm{T}) = f(298\ \mathrm{K}) \exp\left(\left|g\left(\frac{1}{\mathrm{T}} - \frac{1}{298}\right)\right|\right)$$

with the $f(298\ \mathrm{K})$ factor corresponding to the 1σ estimated uncertainty in the room-temperature rate coefficient, $k(298\ \mathrm{K})$, and g is a parameter used to describe the possible increase in uncertainty at temperatures other than 298 K. The uncertainty factor corresponding to the 2σ estimated uncertainty at any temperature is calculated as the square of $f(T)$, i.e., $f(T)^2$.

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Table 3.3. Reaction-rate coefficients and estimated uncertainties for the Cl + compound gas-phase reactions.*

Compound	Chemical Formula	Temperature Range (K) **	*A* *	E/R (K)	*k*(298 K) *	f(298 K)	g	Footnotes
1. CFC-11	CCl_3F	–	*100*	*8960*	*<8.7 (-24)*	–	–	1
2. CFC-12	CCl_2F_2	–	*100*	*11100*	*<5.2 (-27)*	–	–	1
3. CFC-113	CCl_2FCClF_2	–	*100*	*>5480*	*<1.0 (-18)*	–	–	2
4. CFC-114	$CClF_2CClF_2$	–	*100*	*>5480*	*<1.0 (-18)*	–	–	2
5. CFC-115	CF_3CClF_2	–	*100*	*>5480*	*<1.0 (-18)*	–	–	2
6. Carbon Tetrachloride	CCl_4	–	*100*	*5480*	*<1.0 (-18)*	–	–	1
7. Nitrous oxide	N_2O	–	–	–	<1 (-17)			3
8. Halon-1202	CBr_2F_2	–	*100*	*9320*	*<2.6 (-24)*	–	–	1,a
9. Halon-1211	$CBrClF_2$	–	*100*	*6280*	*<7.1 (-20)*	–	–	1
10. Halon-1301	$CBrF_3$	–	*100*	*9290*	*<2.9 (-24)*	–	–	1
11. Halon-2402	$CBrF_2CBrF_2$	–	*100*	*9320*	*<2.6 (-24)*	–	–	1,a
12. Methane	CH_4	181 – 300	7.3	1280	1.0 (-13)	1.05	50	3
13. Methyl Chloroform	CH_3CCl_3	253 – 418	2.86	1716	9.03 (-15)	1.10	100	4,5,b
14. Methyl Chloride	CH_3Cl	222 – 300	19	1100	4.80 (-13)	1.07	50	4,5,c
15. Methyl Bromide	CH_3Br	213 – 300	14	1030	4.40 (-13)	1.05	50	3
16. HCFC-22	$CHClF_2$	298 – 430	5.57	2430	1.60 (-15)	1.08	100	3,5
17. HCFC-141b	CH_3CCl_2F	295 – 429	2.76	2140	2.10 (-15)	1.10	200	4,5,d
18. HCFC-142b	CH_3CClF_2	295 – 429	1.40	2420	4.10 (-16)	1.08	200	4,5,e
19. HFC-23	CHF_3	–	–	–	<5.0 (-16)	–	–	3
20. HFC-32	CH_2F_2	253 – 318	6.93	1590	3.34 (-14)	1.08	100	4,5,f
21. HFC-125	CHF_2CF_3	298	*1.8*	*2600*	3.0 (-16)	1.25	300	3,5
22. HFC-134a	CH_2FCF_3	253 – 300	0.98	1953	1.40 (-15)	1.10	200	4,g
23. HFC-143a	CF_3CH_3	281 – 368	9.7	3760	3.20 (-17)	2	300	4,5,h
24. HFC-152a	CH_3CHF_2	264 – 360	6.3	965	2.5 (-13)	1.10	100	4,i
25. HFC-227ea	CF_3CHFCF_3	298	*2.7*	*2600*	4.39 (-16)	1.30	300	j
26. HFC-245fa	$CHF_2CH_2CF_3$	298	*2.1*	*1700*	6.90 (-15)	1.30	300	k
27. Nitrogen Trifluoride	NF_3	–	*100*	*13200*	<1 (-29)	–	–	1,l

Footnotes

* Estimated values are given in italics; A is in units of 10^{-12} cm^3 molecule^{-1} s^{-1}; k(298 K) is in units of cm^3 molecule^{-1} s^{-1} and (-xx) represents $\times 10^{-xx}$; $k(T) = A \exp(-E/RT)$.

** Temperature range of available experimental data considered in the evaluation of the reaction-rate coefficient parameters and uncertainty limits.

1 No experimental data available for this reaction. The reaction was not evaluated in JPL10-6. The recommendation given here was obtained by setting the pre-exponential factor (A) to 1×10^{-10} cm^3 molecule^{-1} s^{-1} and equating the activation energy (E) to the reaction endothermicity using the thermochemical parameters reported in JPL10-6 and IUPAC.

2 The recommended kinetic parameters are taken to equal to those for the Cl + CCl_4 reaction.

3 A and E/R recommendation is unchanged from JPL10-6.

4 A and E/R recommendation is revised from JPL10-6.

5 f(298 K) and/or g is revised from JPL10-6.

a The rate-coefficient upper limit was estimated with E = 77.5 kJ mol^{-1}, which was obtained from an average of the values for the reaction of Cl with CH_3Br (77.8 kJ mol^{-1}) and CF_3Br (77.2 kJ mol^{-1}).

b The recommended k(298 K) was obtained from an average of the results from the relative-rate studies of Platz *et al.* (1995) and Nilsson *et al.* (2009) and the absolute-rate study of Talhaoui *et al.* (1996). The rate-coefficient temperature dependence was obtained from a fit of the data from Talhaoui *et al.* (1996) and Nilsson *et al.* (2009) after scaling to the recommended k(298 K) value.

c The recommended k(298 K) is an average of the results from Manning and Kurylo (1977), Wallington *et al.* (1990), Beichert *et al.* (1995), Orlando (1999), and Bryukov *et al.* (2002). The rate-coefficient temperature dependence was obtained from a fit of the data from Manning and Kurylo (1977), Wallington *et al.* (1990), Beichert *et al.* (1995), Orlando (1999), Bryukov *et al.* (2002), and Sarzyński *et al.* (2009) for temperatures <300 K.

d The recommended k(298 K) is an average of the results from Wallington and Hurley (1992), Tuazon *et al.*, (1992), Warren and Ravishankara (1993), and Talhaoui *et al.* (1996). The rate-coefficient temperature dependence is based on a fit of the results from the studies of Warren and Ravishankara (<350 K) and Talhaoui *et al.* after scaling to the recommended k(298 K) value.

e The recommended k(298 K) is an average of the results from Wallington and Hurley (1992), Tuazon *et al.* (1992), and Talhaoui *et al.* (1996). The rate-coefficient temperature dependence was taken from Talhaoui *et al.* (1996), which is the only available temperature-dependent study.

f The recommended k(298 K) is an average of the results from Nielsen *et al.* (1992) and Nilsson *et al.* (2009). The rate-coefficient temperature dependence was obtained from a fit of the data from Nielsen *et al.* (1992) and Nilsson *et al.* (2009) for temperatures <300 K after scaling to the recommended k(298 K) value.

g The recommended k(298 K) is an average of the data from Louis *et al.* (1997), Wallington and Hurley (1992), Tuazon *et al.* (1992), Kaiser (1993), and Nilsson *et al.* (2009). The rate-coefficient temperature dependence was obtained by fitting the T <300 K data from Louis *et al.* (1997), Kaiser (1993), and Nilsson *et al.* (2009) after scaling to match the recommended k(298 K) value.

h The recommended k(298 K) is an average of the results from the Tschuikow-Roux *et al.* (1985) and Nielsen *et al.* (1994) relative-rate studies. The rate-coefficient temperature dependence is based on the work of Tschuikow-Roux *et al.* (1985) combined with the rate expression for the $Cl + CH_4$ reaction recommended in this report.

i The recommended A and E/R values are for the total rate coefficient, i.e., loss of HFC-152a. The recommended k(298 K) was obtained from an average of one absolute-rate and four relative-rate studies, which are in good agreement. The temperature dependence was taken from Yano and Tschuikow-Roux (1986) where the site-specific rate coefficients are given as
$Cl + CH_3CHF_2 \rightarrow HCl + CH_3CF_2$; $k(T) = 6.3 \times 10^{-12} \exp(-965/T)$ cm^3 molecule^{-1} s^{-1}
$Cl + CH_3CHF_2 \rightarrow HCl + CH_2CHF_2$; $k(T) = 7.0 \times 10^{-12} \exp(-2400/T)$ cm^3 molecule^{-1} s^{-1}

j The recommended k(298 K) is the average of the relative-rate determinations by Møgelberg *et al.* (1996) and E/R was estimated by comparison with compounds having similar reactivity at 298 K (e.g., HFC-125). The reaction was not evaluated in JPL10-6.

k The recommended k(298 K) was taken from Chen *et al.* (1997) and E/R was estimated by comparison with compounds having similar reactivity at 298 K (e.g., CH_3CCl_3). The reaction was not evaluated in JPL10-6.

l F atom abstraction from NF_3 by Cl is slightly exothermic (Gurvich *et al.*, 1989), ca. -11 kJ mol^{-1}. A G3B3 quantum chemical method (Curtiss *et al.*, 2001) calculation predicts an activation barrier (E/R) of ~110 kJ mol^{-1} for this reaction. Assuming a pre-exponential factor (A) of 1×10^{-10} cm^3 molecule^{-1} s^{-1} and this activation barrier provides the bases of the recommendation.

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1. $CFCl_3$ (CFC-11)

Recommended Rate Coefficient
$k(T) < 1 \times 10^{-10} \exp(-8960/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 8.7 \times 10^{-24}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommendation given here was obtained by setting the pre-exponential factor (A) to 1×10^{-10} cm^3 molecule^{-1} s^{-1}; this is a conservative upper limit based on the range of A factors found for Cl + halocarbon reactions (values are typically in the range (0.1-2.0) $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1}), and equating the activation energy (E) to the reaction endothermicity calculated using the thermochemical parameters reported in the JPL10-6 and IUPAC data evaluations.

2. CF_2Cl_2 (CFC-12)

Recommended Rate Coefficient
$k(T) < 1 \times 10^{-10} \exp(-11100/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 5.2 \times 10^{-27}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommendation given here was obtained by setting the pre-exponential factor (A) to 1×10^{-10} cm^3 molecule^{-1} s^{-1}; this is a conservative upper limit based on the range of A factors found for Cl + halocarbon reactions (values are typically in the range (0.1-2.0) $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1}), and equating the activation energy (E) to the reaction endothermicity calculated using the thermochemical parameters reported in the JPL10-6 and IUPAC data evaluations.

3. CCl_2FCClF_2 (CFC-113)

Recommended Rate Coefficient
$k(T) < 1 \times 10^{-10} \exp(-5480/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 1.0 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommended rate coefficient Arrhenius parameters are taken to be equal to those for the Cl + CCl_4 reaction.

4. $CClF_2CClF_2$ (CFC-114)

Recommended Rate Coefficient
$k(T) < 1 \times 10^{-10} \exp(-5480/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 1.0 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommended rate coefficient Arrhenius parameters are taken to be equal to those for the Cl + CCl_4 reaction.

5. CF_3CClF_2 (CFC-115)

Recommended Rate Coefficient
$k(T) < 1 \times 10^{-10} \exp(-5480/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 1.0 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommended rate coefficient Arrhenius parameters are taken to be equal to those for the Cl + CCl_4 reaction.

6. CCl_4 (Carbon Tetrachloride)

Recommended Rate Coefficient
$k(T) < 1 \times 10^{-10} \exp(-5480/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 1.0 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommendation given here was obtained by setting the pre-exponential factor (A) to 1×10^{-10} cm^3 molecule^{-1} s^{-1}; this is a conservative upper limit based on the range of A factors found for Cl + halocarbon reactions (values are typically in the range (0.1-2.0) $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1}), and equating the activation energy (E) to the reaction endothermicity calculated using the thermochemical parameters reported in the JPL10-6 and IUPAC data evaluations.

7. N_2O (Nitrous oxide)

Recommended Rate Coefficient
$k(298\ K) < 1.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}

The recommendation is unchanged from JPL10-6.

The rate coefficient was been determined in a single high temperature, ~1000 K, study. The largest reported value was 10^{-17} cm^3 molecule^{-1} s^{-1} with an activation energy of 142 kJ mol^{-1}.

8. CBr_2F_2 (Halon-1202)

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-10} \exp(-9320/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) < 2.6 \times 10^{-24}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommendation given here was obtained by setting the pre-exponential factor (A) to 1×10^{-10} cm^3 molecule^{-1} s^{-1}; this is a conservative upper limit based on the range of A factors found for Cl + halocarbon reactions (values are typically in the range (0.1-2.0) $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1}), and equating the activation energy (E) to the reaction endothermicity calculated using the thermochemical parameters reported in the JPL10-6 and IUPAC data evaluations.

9. $CBrClF_2$ (Halon-1211)

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-10} \exp(-6280/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) < 7.1 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommendation given here was obtained by setting the pre-exponential factor (A) to 1×10^{-10} cm^3 molecule^{-1} s^{-1}; this is a conservative upper limit based on the range of A factors found for Cl + halocarbon reactions (values are typically in the range (0.1-2.0) $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1}), and equating the activation energy (E) to the reaction endothermicity calculated using the thermochemical parameters reported in the JPL10-6 and IUPAC data evaluations.

10. $CBrF_3$ (Halon-1301)

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-10} \exp(-9290/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) < 2.9 \times 10^{-24}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommendation given here was obtained by setting the pre-exponential factor (A) to 1×10^{-10} cm^3 molecule^{-1} s^{-1}; this is a conservative upper limit based on the range of A factors found for Cl + halocarbon reactions (values are typically in the range (0.1-2.0) $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1}), and equating the activation energy (E) to the reaction endothermicity calculated using the thermochemical parameters reported in the JPL10-6 and IUPAC data evaluations.

11. $CBrF_2CBrF_2$ (Halon-2402)

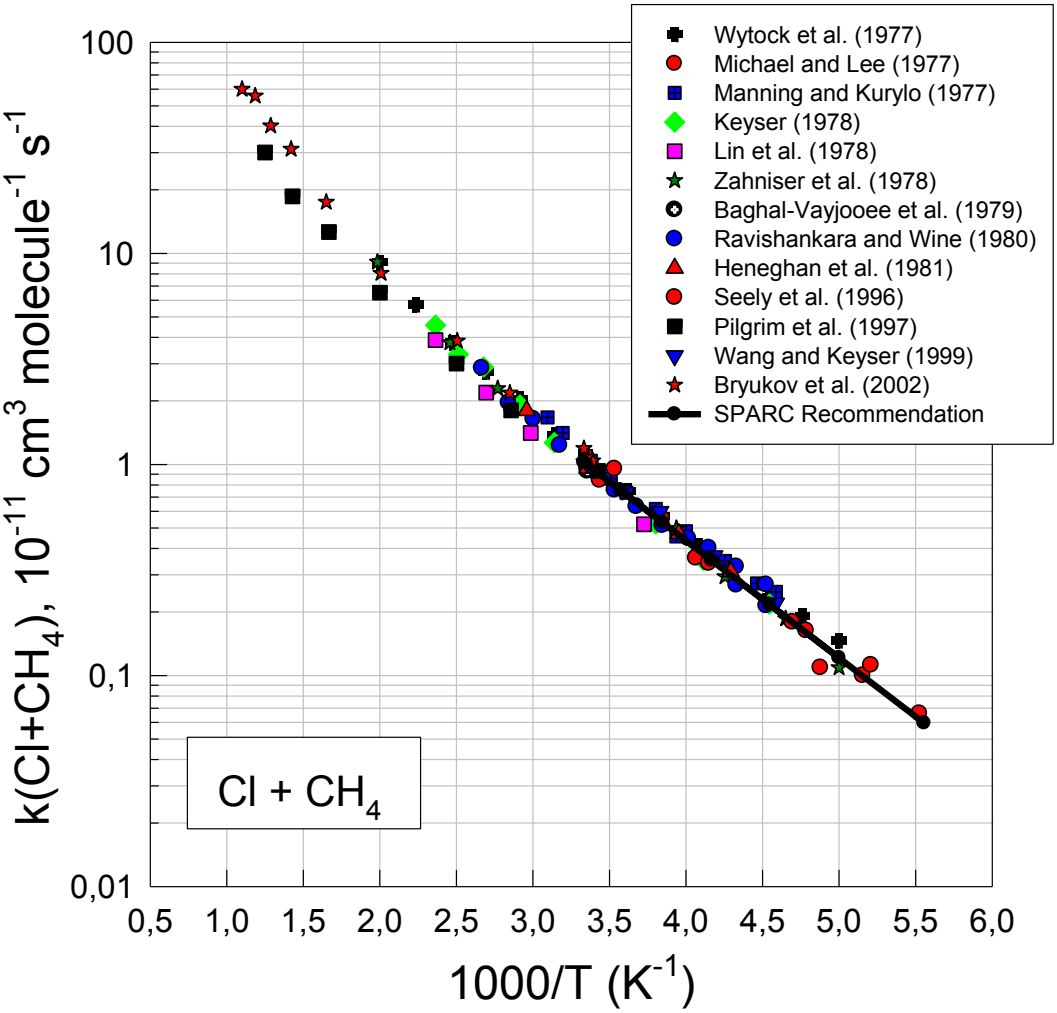
Recommended Rate Coefficient

$k(T) < 1 \times 10^{-10} \exp(-9320/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) < 2.6 \times 10^{-24}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction and the reaction was not evaluated in JPL10-6. The recommendation given here was obtained by setting the pre-exponential factor (A) to 1×10^{-10} cm^3 molecule^{-1} s^{-1}; this is a conservative upper limit based on the range of A factors found for Cl + halocarbon reactions (values are typically in the range (0.1-2.0) $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1}), and equating the activation energy (E) to the reaction endothermicity calculated using the thermochemical parameters reported in the JPL10-6 and IUPAC data evaluations.

12. CH_4 (Methane)



For clarity, not all available data are plotted (see JPL-10-6)

Recommended Rate Coefficient

$k(T) = 7.3 \times 10^{-12} \exp(-1280/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.05$

$g = 50$

$k(298)$, A, and E/R recommendation are unchanged from JPL10-6.
$f(298\ K)$ and g are unchanged from JPL10-6.

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Rate-coefficient data for the Cl + CH_4 reaction from the following studies is not included in the attached figure (see JPL10-6 for further details):

Beichert, P., J. L. Wingen, R. Vogt, M. J. Ezell, M. Ragains, R. Neavyn, and B. J. Finlayson-Pitts, Rate constants for the reactions of chlorine atoms with some simple alkanes at 298 K: Measurement of a self-consistent set using both absolute and relative rate methods, *J. Phys. Chem.*, *99*, 13156-13162, 1995.

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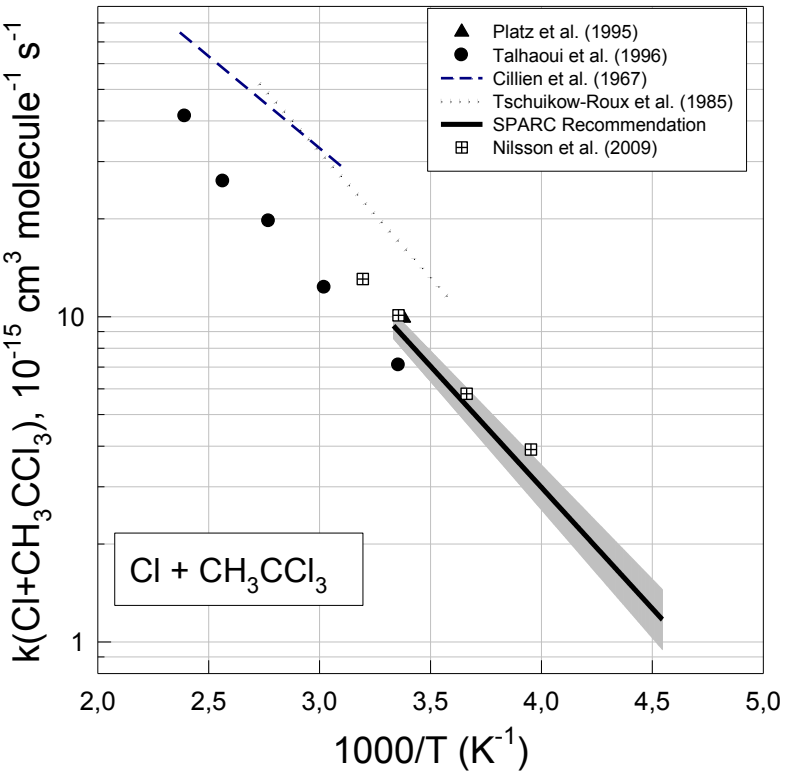
13. CH_3CCl_3



Recommended Rate Coefficient

$k(T) = 2.86 \times 10^{-12} \exp(-1716/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\text{ K}) = 9.03 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.10$

$g = 100$

$k(298)$, A, and E/R recommendations are revised from JPL10-6.
$f(298\text{ K})$ and g are revised from JPL10-6.

References

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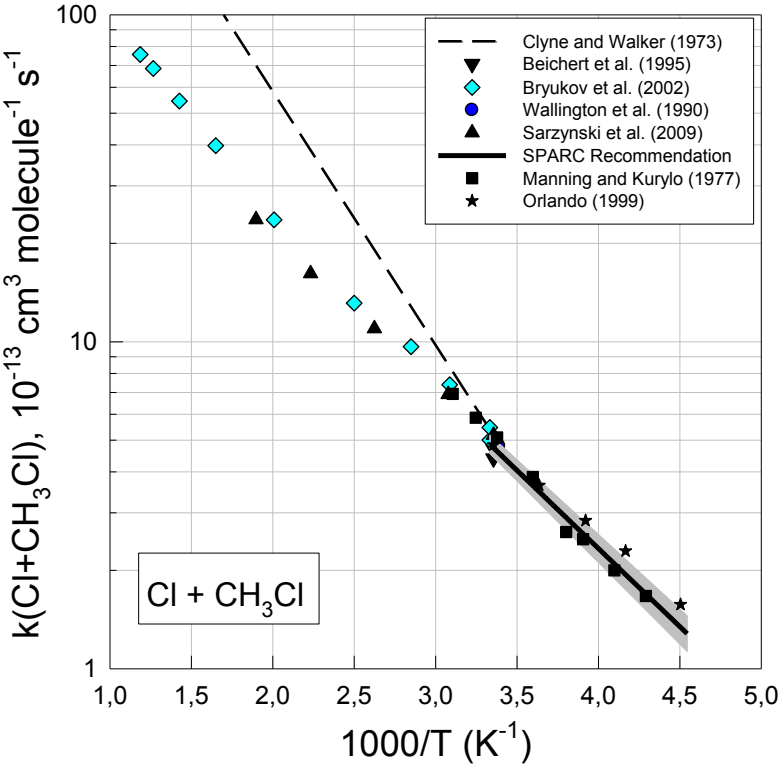
Talhaoui, A., F. Louis, P. Devolder, B. Meriaux, J. P. Sawerysyn, and M. T. Rayez, Rate coefficients of the reactions of chlorine atoms with haloethanes of type $CH_3CCl_{3-x}F_x$ (x = 0, 1, and 2): Experimental and ab initio theoretical studies, *J. Phys. Chem.*, *100*, 13531-13538, 1996.

Tschuikow-Roux, E., T. Yano, and J. Niedzielski, Reactions of ground state chlorine atoms with fluorinated methanes and ethanes, *J. Chem. Phys.*, *82*, 65-74, 1985.

14. CH_3Cl



Recommended Rate Coefficient

$k(T) = 1.9 \times 10^{-11} \exp(-1100/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.07$

$g = 50$

$k(298)$, A, and E/R recommendations are revised from JPL10-6.
$f(298\ K)$ and g are unchanged from JPL10-6.

References

Beichert, P., J. L. Wingen, R. Vogt, M. J. Ezell, M. Ragains, R. Neavyn, and B. J. Finlayson-Pitts, Rate constants for the reactions of chlorine atoms with some simple alkanes at 298 K: Measurement of a self-consistent set using both absolute and relative rate methods, *J. Phys. Chem.*, *99*, 13156-13162, 1995.

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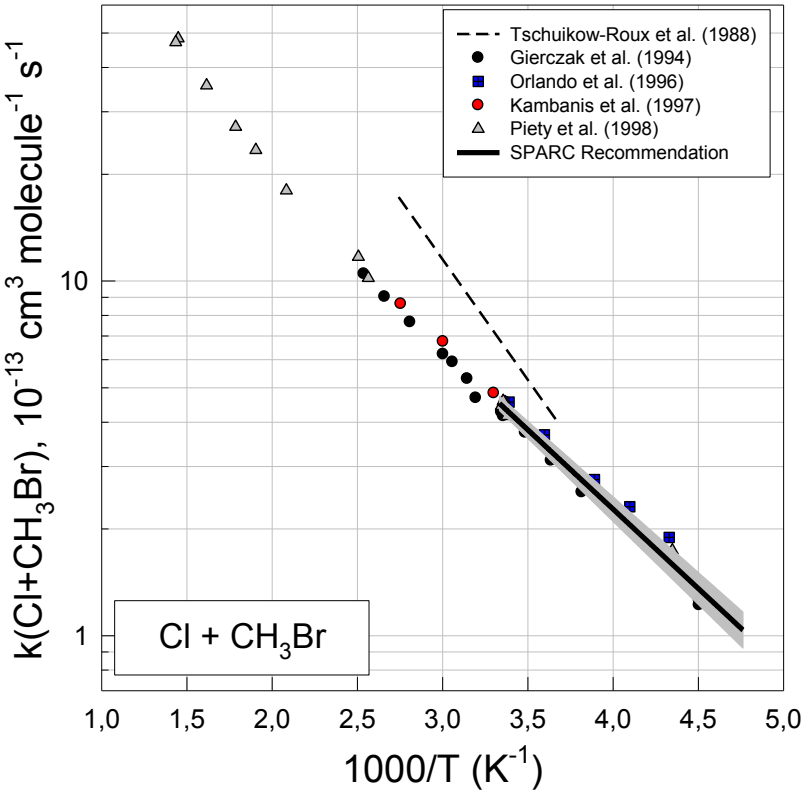
15. CH_3Br



Recommended Rate Coefficient

$k(T) = 1.4 \times 10^{-11} \exp(-1030/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) = 4.40 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.05$

$g = 50$

$k(298)$, A, and E/R recommendations unchanged from JPL10-6.
$f(298\ K)$ and g are unchanged from JPL10-6.

References

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Orlando, J. J., G. S. Tyndall, T. J. Wallington, and M. Dill, Atmospheric chemistry of CH_2Br_2: Rate coefficients for its reaction with Cl atoms and OH and the chemistry of the $CHBr_2O$ radical, *Int. J. Chem. Kinet.*, *28*, 433-442, 1996.

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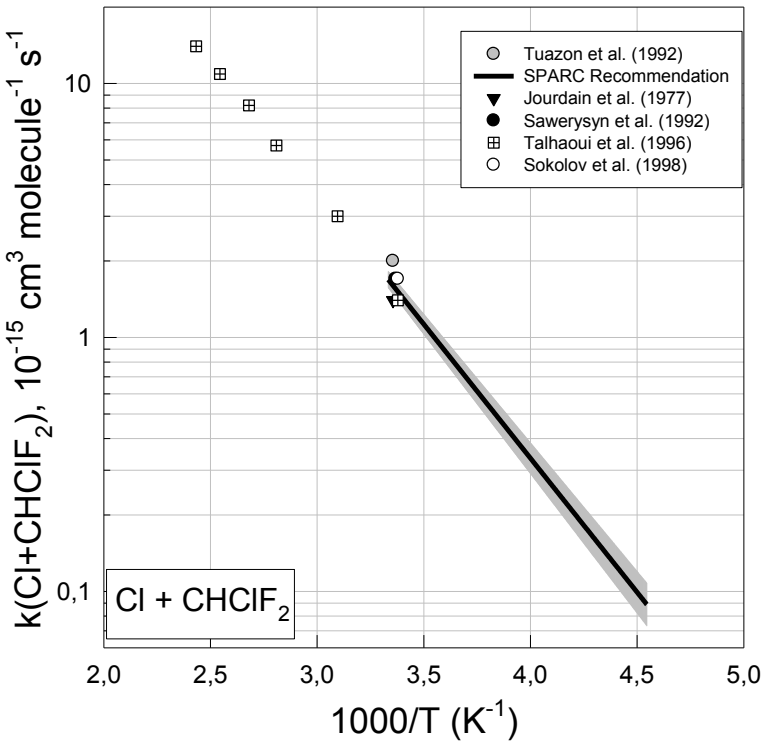
16. HCFC-22 ($CHClF_2$)



Recommended Rate Coefficient

$k(T) = 5.57 \times 10^{-12} \exp(-2430/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\text{ K}) = 1.60 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.08$

$g = 100$

$k(298)$, A, and E/R recommendations are unchanged from JPL10-6.
$f(298\text{ K})$ and g are revised from JPL10-6.

References

Jourdain, G. L., G. Poulet, J. Barassin, G. Le Bras, and J. Combourieu, Mécanismes chimiques de la pollution atmosphérique par les composés halogènes: Étude cinétique des réactions élémentaires possibles, *J. Pollut. Atmos.*, *75*, 256-259, 1977.

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Sokolov, O., M. D. Hurley, T. J. Wallington, E. W. Kaiser, J. Platz, O. J. Nielsen, F. Berho, M.-T. Rayez, and R. Lesclaux, Kinetics and mechanism of the gas-phase reaction of Cl atoms with benzene, *J. Phys. Chem. A*, *102*, 10671-10681, 1998.

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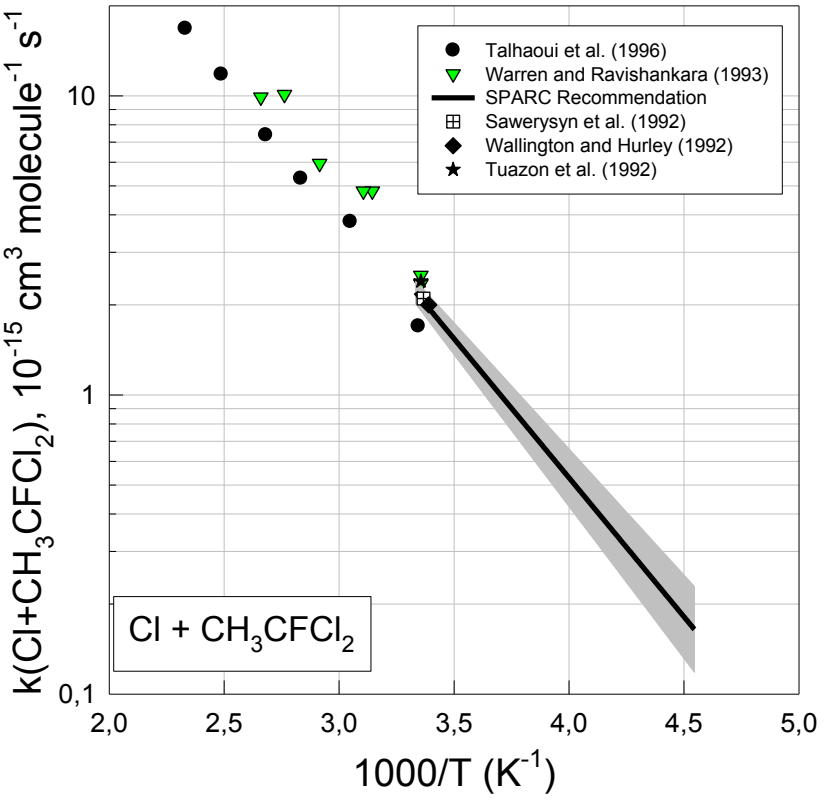
17. HCFC-141b (CH_3CFCl_2)



Recommended Rate Coefficient

$k(T) = 2.76 \times 10^{-12} \exp(-2140/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) = 2.10 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.10$

$g = 200$

A and *E*/R recommendations are revised from JPL10-6.
f(298 K) is revised and *g* is unchanged from JPL10-6.

References

Sawerysyn, J. P., A. Talhaoui, B. Meriaux, and P. Devolder, Absolute rate constants for elementary reactions between chlorine atoms and CHF_2Cl, CH_3CFCl_2, CH_3CF_2Cl and CH_2FCF_3 at 297 ± 2 K, *Chem. Phys. Lett.*, *198*, 197-199, 1992.

Talhaoui, A., F. Louis, P. Devolder, B. Meriaux, J. P. Sawerysyn, and M. T. Rayez, Rate coefficients of the reactions of chlorine atoms with haloethanes of type $CH_3CCl_{3-x}F_x$ (x = 0, 1, and 2): Experimental and ab initio theoretical studies, *J. Phys. Chem.*, *100*, 13531-13538, 1996.

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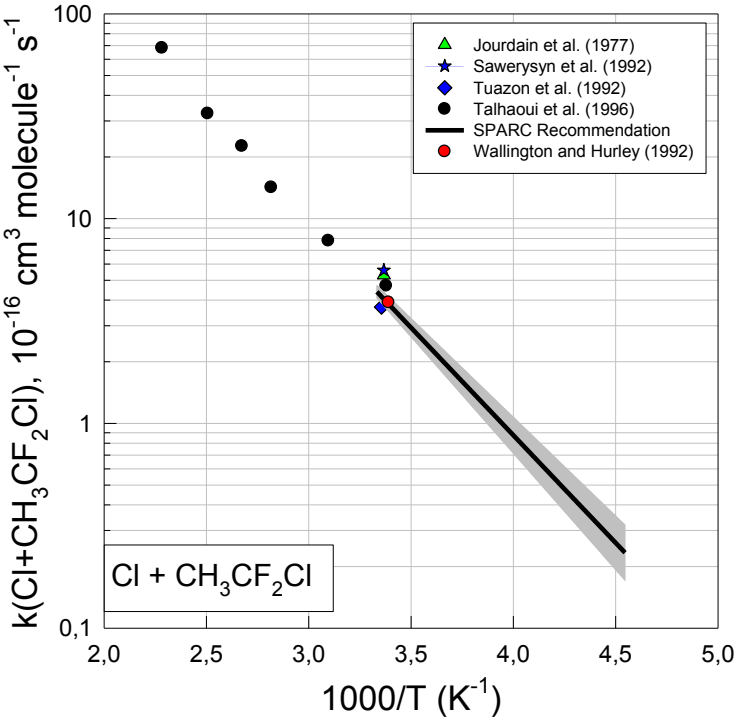
Wallington, T. J., and M. D. Hurley, A kinetic study of the reaction of chlorine atoms with CF_3CHCl_2, CF_3CH_2F, $CFCl_2CH_3$, CF_2ClCH_3, CHF_2CH_3, CH_3D, CH_2D_2, CHD_3, CD_4, and CD_3Cl at 295 ± 2 K, *Chem. Phys. Lett.*, *189*, 437-442, 1992.

Warren, R. F., and A. R. Ravishankara, Kinetics of Cl(^{2}P) reactions with CF_3CHCl_2, CF_3CHFCl, and CH_3CFCl_2, *Int. J. Chem. Kinet.*, *25*, 833-844, 1993.

18. HCFC-142b (CH_3CClF_2)



Recommended Rate Coefficient

$k(T) = 1.40 \times 10^{-12} \exp(-2420/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) = 4.10 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.08$

$g = 200$

$k(298)$, A, and E/R recommendations are revised from JPL10-6.
$f(298\ K)$ is revised and g is unchanged from JPL10-6.

References

Jourdain, G. L., G. Poulet, J. Barassin, G. Le Bras, and J. Combourieu, Mécanismes chimiques de la pollution atmosphérique par les composés halogènes: Étude cinétique des réactions élémentaires possibles, *J. Pollut. Atmos.*, *75*, 256-259, 1977.

Sawerysyn, J. P., A. Talhaoui, B. Meriaux, and P. Devolder, Absolute rate constants for elementary reactions between chlorine atoms and CHF_2Cl, CH_3CFCl_2, CH_3CF_2Cl and CH_2FCF_3 at 297 ± 2 K, *Chem. Phys. Lett.*, *198*, 197-199, 1992.

Talhaoui, A., F. Louis, P. Devolder, B. Meriaux, J. P. Sawerysyn, and M. T. Rayez, Rate coefficients of the reactions of chlorine atoms with haloethanes of type $CH_3CCl_{3-x}F_x$ (x = 0, 1, and 2): Experimental and ab initio theoretical studies, *J. Phys. Chem.*, *100*, 13531-13538, 1996.

Tuazon, E. C., R. Atkinson, and S. B. Corchnoy, Rate constants for the gas-phase reactions of Cl atoms with a series of hydrofluorocarbons and hydrochlorofluorocarbons at 298 ± 2 K, *Int. J. Chem. Kinet.*, *24*, 639-648, 1992.

Wallington, T. J., and M. D. Hurley, A kinetic study of the reaction of chlorine atoms with CF_3CHCl_2, CF_3CH_2F, $CFCl_2CH_3$, CF_2ClCH_3, CHF_2CH_3, CH_3D, CH_2D_2, CHD_3, CD_4, and CD_3Cl at 295 ± 2 K, *Chem. Phys. Lett.*, *189*, 437-442, 1992.

19. CHF_3 (HFC-23)

Recommended Rate Coefficient

$k(298\ K) < 5 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}

Recommendation is unchanged from JPL10-6.

References

Coomber, J. W., and E. Whittle, Photochlorination of methane and fluoroform: Dissociation energy D(CF_3-H) and entropy of CF_3 radical, *Trans. Faraday Soc.*, 62, 2183-2190, 1966.

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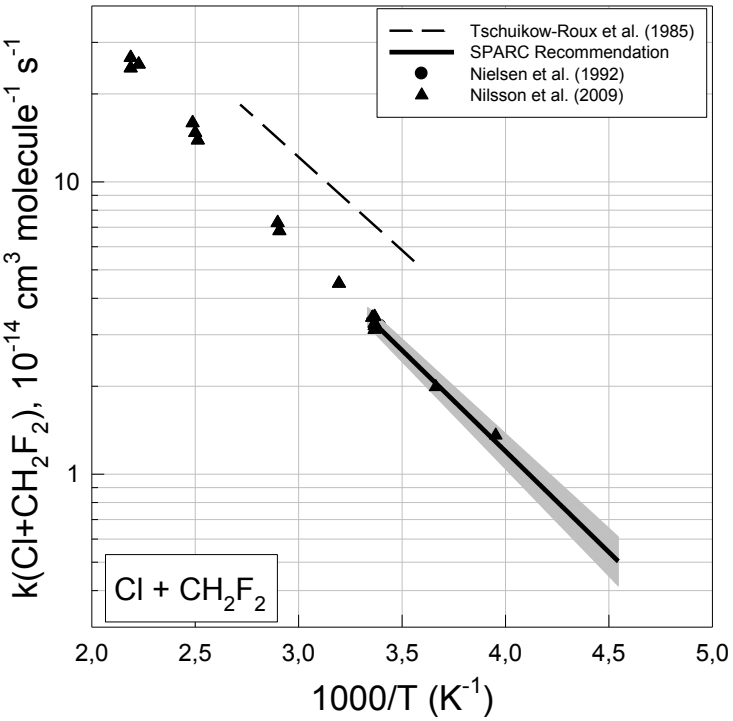
20. HFC-32 (CH_2F_2)



Recommended Rate Coefficient

$k(T) = 6.93 \times 10^{-12} \exp(-1590/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\text{ K}) = 3.34 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.08$

$g = 100$

$k(298)$, A, and E/R recommendations are revised from JPL10-6.
$f(298\text{ K})$ and g are revised from JPL10-6.

References

Nielsen, O. J., T. Ellermann, E. Bartkiewicz, T. J. Wallington, and M. D. Hurley, UV absorption spectra, kinetics and mechanisms of the self-reaction of CHF_2O_2 radicals in the gas phase at 298 K, *Chem. Phys. Lett.*, *192*, 82-88, 1992.

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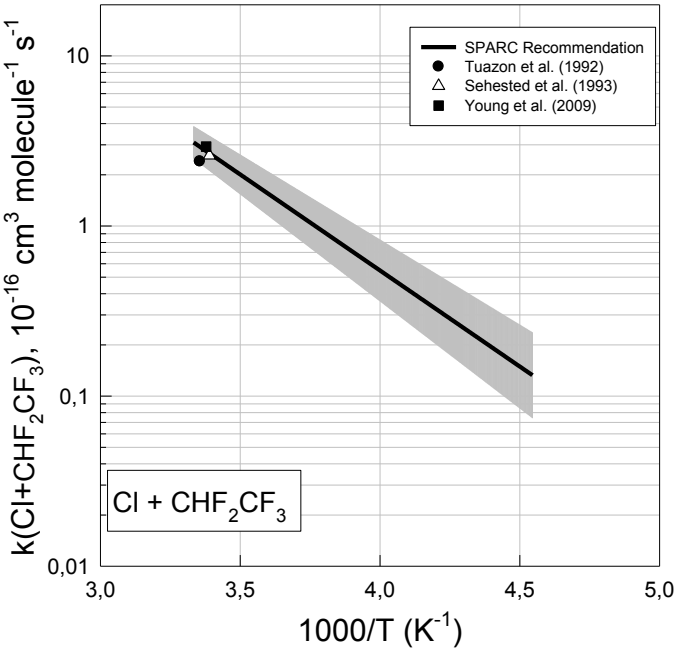
21. HFC-125 (CHF_2CF_3)



Recommended Rate Coefficient

$k(T) = 1.8\times10^{-12} \exp(-2600/T)$ cm^3 molecule^{-1} s^{-1}

$k(298) = 3.0\times10^{-16}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.25$

$g = 300$

$k(298)$, A, and E/R recommendations are unchanged from JPL10-6.
$f(298\ K)$ is revised and g is unchanged from JPL10-6.

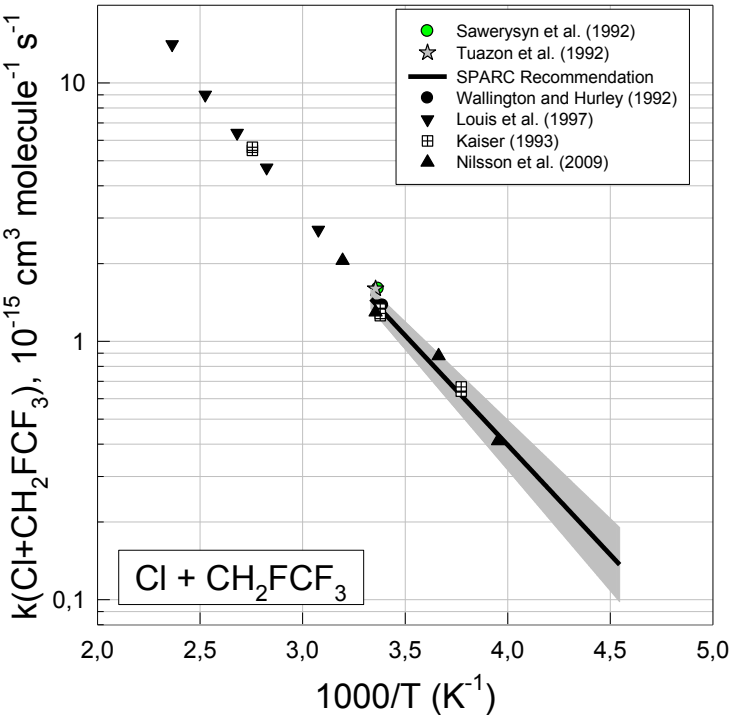
References

Sehested, J., T. Ellermann, O. J. Nielsen, T. J. Wallington, and M. D. Hurley, UV absorption spectrum, and kinetics and mechanism of the self reaction of $CF_3CF_2O_2$ radicals in the gas phase at 295 K, *Int. J. Chem. Kinet.*, *25*, 701-717, 1993.

Tuazon, E. C., R. Atkinson, and S. B. Corchnoy, Rate constants for the gas-phase reactions of Cl atoms with a series of hydrofluorocarbons and hydrochlorofluorocarbons at 298 ± 2 K, *Int. J. Chem. Kinet.*, *24*, 639-648, 1992.

Young, C. J., M. D. Hurley, T. J. Wallington, and S. A. Mabury, Atmospheric chemistry of CF_3CF_2H and $CF_3CF_2CF_2CF_2H$: Kinetics and products of gas-phase reactions with Cl atoms and OH radicals, infrared spectra, and formation of perfluorocarboxylic acids, *Chem. Phys. Lett.*, *473*, 251-256, 2009.

22. HFC-134a (CH_2FCF_3)



Recommended Rate Coefficient

$k(T) = 9.8 \times 10^{-13} \exp(-1953/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\text{ K}) = 1.40 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.10$

$g = 200$

$k(298)$, A, and E/R recommendations are revised from JPL10-6.
$f(298\text{ K})$ and g are unchanged from JPL10-6.

References

Kaiser, E. W., Relative rate constants for reactions of HFC 152a, 143, 143a, 134a, and HCFC 124 with F or Cl atoms and for CF_2CH_3, CF_2HCH_2, and CF_3CFH radicals with F_2, Cl_2, and O_2, *Int. J. Chem. Kinet.*, *25*, 667-680, 1993.

Louis, F., A. Talhaoui, J. P. Sawerysyn, M.-T. Rayez, and J.-C. Rayez, Rate coefficients for the gas phase reactions of CF_3CH_2F (HFC-134a) with chlorine and fluorine atoms: Experimental and *ab Initio* theoretical Studies, *J. Phys. Chem. A*, *101*, 8503-8507, 1997.

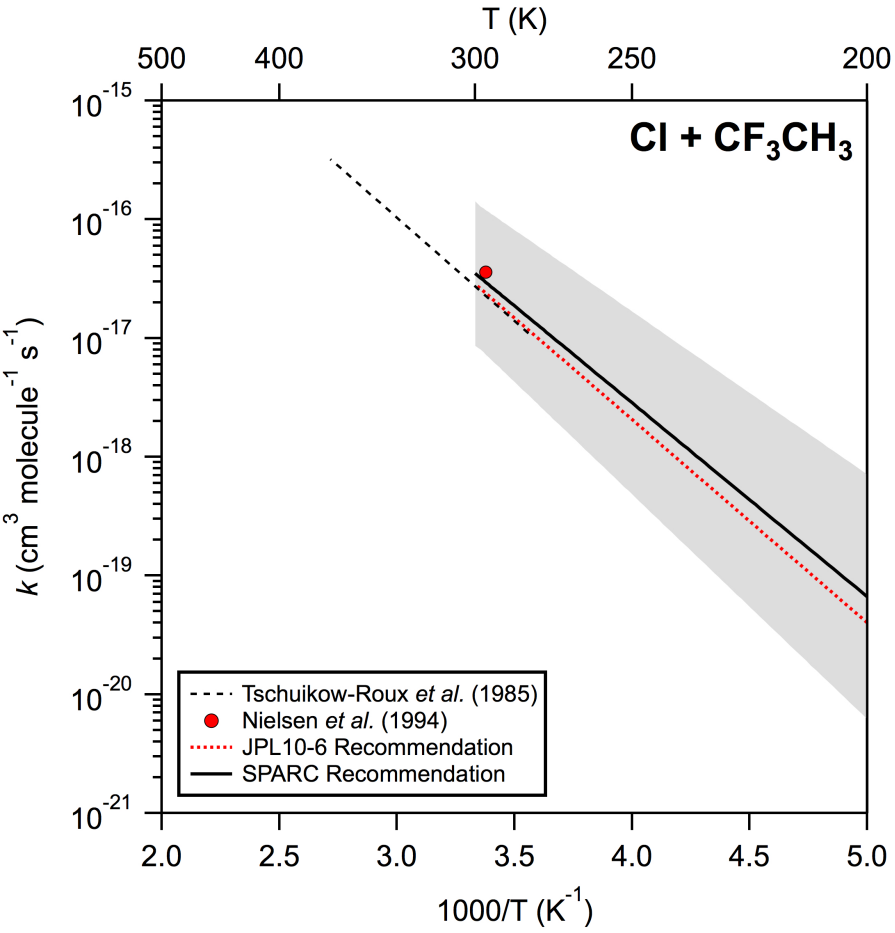
Nilsson, E. J. K., M. S. Johnson, O. J. Nielsen, E. W. Kaiser, and T. J. Wallington, Kinetics of the gas-phase reactions of chlorine atoms with CH_2F_2, CH_3CCl_3, and CF_3CFH_2 over the temperature range 253-553 K, *Int. J. Chem. Kinet.*, *41*, 401-406, 2009.

Sawerysyn, J. P., A. Talhaoui, B. Meriaux, and P. Devolder, Absolute rate constants for elementary reactions between chlorine atoms and CHF_2Cl, CH_3CFCl_2, CH_3CF_2Cl and CH_2FCF_3 at 297 ± 2 K, *Chem. Phys. Lett.*, *198*, 197-199, 1992.

Tuazon, E. C., R. Atkinson, and S. B. Corchnoy, Rate constants for the gas-phase reactions of Cl atoms with a series of hydrofluorocarbons and hydrochlorofluorocarbons at 298 ± 2 K, *Int. J. Chem. Kinet.*, *24*, 639-648, 1992.

Wallington, T. J., and M. D. Hurley, A kinetic study of the reaction of chlorine atoms with CF_3CHCl_2, CF_3CH_2F, $CFCl_2CH_3$, CF_2ClCH_3, CHF_2CH_3, CH_3D, CH_2D_2, CHD_3, CD_4, and CD_3Cl at 295 ± 2 K, *Chem. Phys. Lett.*, *189*, 437-442, 1992.

23. HFC-143a (CH_3CF_3)



Recommended Rate Coefficient

$k(T) = 9.7 \times 10^{-12} \exp(-3760/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) = 3.20 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 2$

$g = 300$

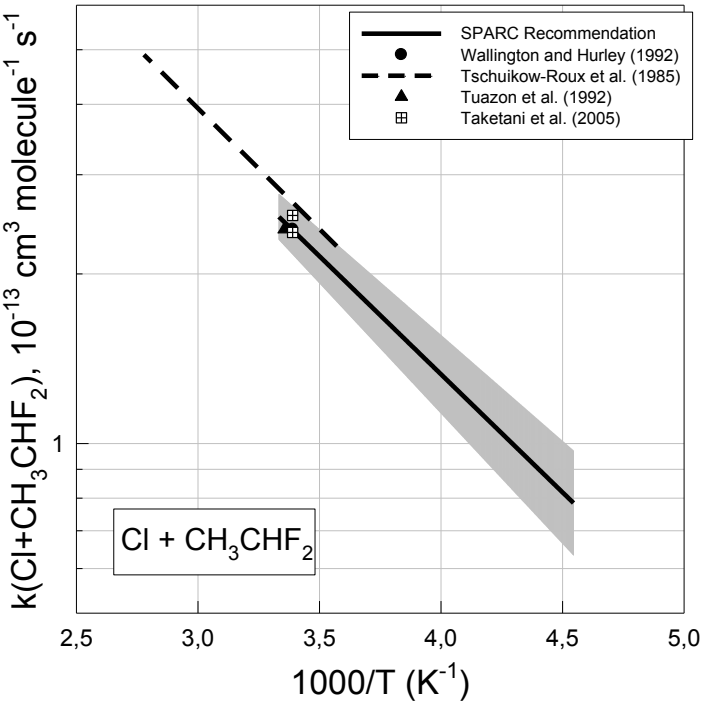
$k(298)$, A, and E/R recommendations are revised from JPL10-6.
$f(298\ K)$ is revised and g is unchanged from JPL10-6.

References

Nielsen, O. J., E. Gamborg, J. Sehested, T. J. Wallington, and M. D. Hurley, Atmospheric chemistry of HFC-143a: Spectokinetic investigation of the $CF_3CH_2O_2$ radical, its reactions with NO and NO_2, and the fate of CF_3CH_2O, *J. Phys. Chem.*, *98*, 9518-9525, 1994.

Tschuikow-Roux, E., T. Yano, and J. Niedzielski, Reactions of ground state chlorine atoms with fluorinated methanes and ethanes, *J. Chem. Phys.*, *82*, 65-74, 1985.

24. HFC-152a (CH_3CHF_2)



Recommended Rate Coefficient

$k(T) = 6.3 \times 10^{-12} \exp(-965/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\text{ K}) = 2.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.10$

$g = 100$

$k(298)$, A, and E/R recommendations are revised from JPL10-6.
$f(298\text{ K})$ and g are unchanged from JPL10-6.

References

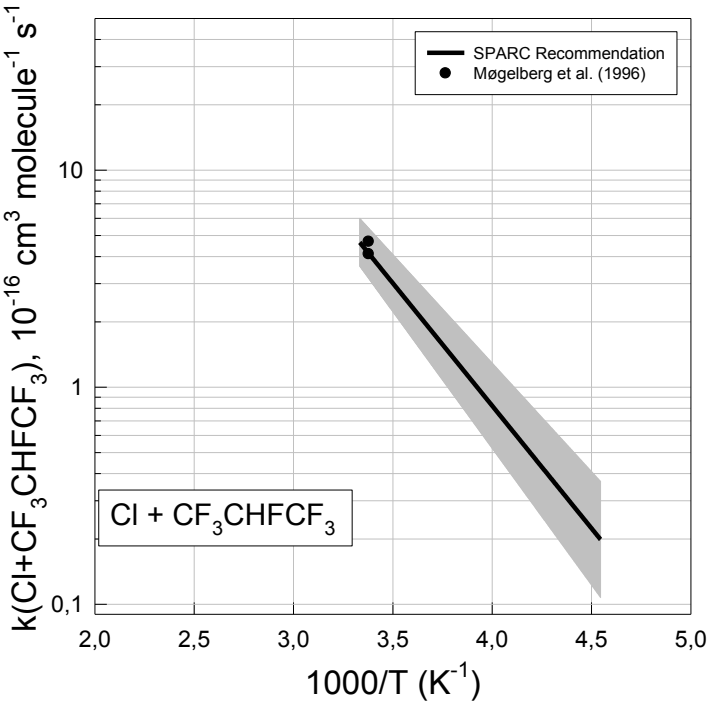
Taketani, F., T. Nakayama, K. Takahashi, Y. Matsumi, M.D. Hurley, T.J. Wallington, A. Toft, and M.P. Andersen, Atmospheric chemistry of CH_3CHF_2 (HFC-152a): Kinetics, mechanisms, and products of Cl atom- and OH radical-initiated oxidation in the presence and absence of NO_x, *J. Phys. Chem. A*, *109*, 9061-9069, 2005.

Tschuikow-Roux, E., T. Yano, and J. Niedzielski, Reactions of ground state chlorine atoms with fluorinated methanes and ethanes, *J. Chem. Phys.*, *82*, 65-74, 1985.

Tuazon, E. C., R. Atkinson, and S. B. Corchnoy, Rate constants for the gas-phase reactions of Cl atoms with a series of hydrofluorocarbons and hydrochlorofluorocarbons at 298 ± 2 K, *Int. J. Chem. Kinet.*, *24*, 639-648, 1992.

Wallington, T. J., and M. D. Hurley, A kinetic study of the reaction of chlorine atoms with CF_3CHCl_2, CF_3CH_2F, $CFCl_2CH_3$, CF_2ClCH_3, CHF_2CH_3, CH_3D, CH_2D_2, CHD_3, CD_4, and CD_3Cl at 295 ± 2 K, *Chem. Phys. Lett.*, *189*, 437-442, 1992.

25. HFC-227ea (CF_3CHFCF_3)



Recommended Rate Coefficient

$k(T) = 2.7 \times 10^{-12} \exp(-2600/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) = 4.39 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.30$

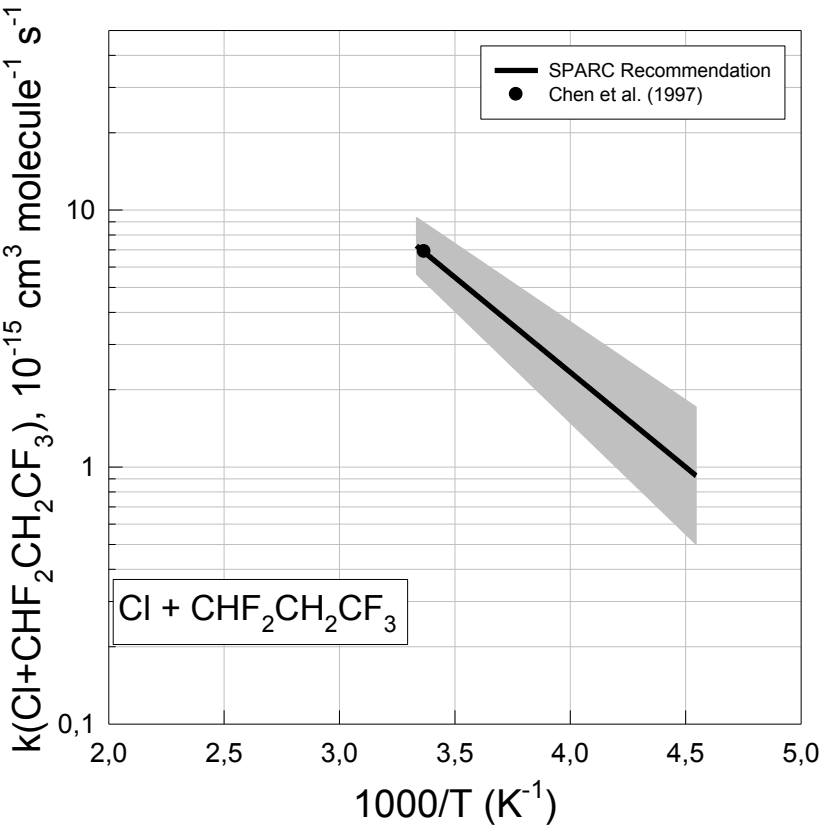
$g = 300$

The reaction was not evaluated in JPL10-6.

Reference

Møgelberg, T. E., J. Sehested, M. Bilde, T. J. Wallington, and O. J. Nielsen, Atmospheric chemistry of CF_3CFHCF_3 (HFC-227ea): Spectrokinetic investigation of the $CF_3CFO_2CF_3$ radical, its reactions with NO and NO_2, and fate of the CF_3CFOCF_3 radicals, *J. Phys. Chem.*, *100,* 8882-8889, 1996.

26. HFC-245fa ($CHF_2CH_2CF_3$)



Recommended Rate Coefficient

$k(T) = 2.1 \times 10^{-12} \exp(-1700/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) = 6.90 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298) = 1.30$

$g = 300$

The reaction was not evaluated in JPL10-6.

Reference

Chen, J., V. Young, and H. Niki, Kinetic and mechanistic studies for reactions of $CF_3CH_2CHF_2$ (HFC-245fa) initiated by H-atom abstraction using atomic chlorine, *J. Phys. Chem. A*, *101,* 2648-2653, 1997.

27. NF_3

Recommended Rate Coefficient
$k(T) < 1 \times 10^{-10} \exp(-13200/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 1 \times 10^{-29}$ cm^3 molecule^{-1} s^{-1}

No experimental data are available for this reaction.
The reaction was not evaluated in JPL10-6.[1]

F atom abstraction from NF_3 by Cl atom is slightly exothermic (Gurvich *et al.*, 1989), ca. -11 kJ mol^{-1}. A G3B3 quantum chemical method (Curtiss *et al.*, 2001) calculation yields a similar exothermicity for this reaction, -8.5 kJ mol^{-1}. Hence, E/R can't simply be estimated from the reaction thermochemistry. A G3B3 quantum chemical method calculation of the reaction activation barrier (E/R) yields a value of ~110 kJ mol^{-1}. Assuming a pre-exponential factor of 1×10^{-10} cm^3 molecule^{-1} s^{-1} and the calculated activation barrier provides the basis of the recommendation.

References

Curtiss, L. A., P. C. Redfern, K. Raghavachari, and J. A. Pople, Gaussian-3X (G3X) theory: Use of improved geometries, zero-point energies, and Hartree-Fock basis sets, *J. Chem. Phys.*, *114*, 108-117, 2001.

Gurvich, L. V., I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, Fourth Edition, Hemisphere Pub. Co., New York, 1989.