Chapter 3 – Supplement 1

Evaluation of Atmospheric Loss Processes: OH Kinetics Supplement

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Rate coefficients for the reaction of the OH radical with the compounds included in the SPARC Lifetime report have received various amounts of attention. The figures included in this supplement contain (1) a summary of the available literature data for each reaction, (2) the SPARC recommendation for the OH reaction-rate coefficient (solid line) and the basis of the recommendation, and (3) the 2σ uncertainty range in the recommended reaction-rate coefficient shown as the shaded area. The original (un-normalized) experimental data are plotted in the figures unless noted otherwise. The recommended temperature dependence, E/R, was determined from fits of data normalized to the recommended k(298 K), hence, some of the plotted data used in the fits may not appear to be in agreement with the shaded area of the recommended fit.

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

Fully halogenated compounds do not undergo measureable reaction with OH at atmospheric temperatures. Upper limits of the rate coefficients for the reactions of CFCs (CCl_3F, CCl_2F_2, CCl_2FCClF_2, $CClF_2CClF_2$, CF_3CClF_2, and CCl_4) were estimated based on thermochemistry by equating the activation energy with the reaction endothermicity[1,2] for the abstraction of a Cl atom and assuming an Arrhenius pre-exponential factor of 1×10^{-11} cm^3 molecule^{-1} s^{-1}. The corresponding estimations for the reactions of Halons ($CBrClF_2$, $CBrF_3$, CBr_2F_2, and $CBrF_2CBrF_2$) are based on the upper limits of the rate coefficients experimentally obtained above room temperature assuming an Arrhenius pre-exponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1}.

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(1) Sander, S., 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, and P. H. Wine, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 17, JPL Publication 10-6*, Jet Propulsion Laboratory, California Institute of Technology, 2011.

(2) Atkinson, R., D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, and T. J. Wallington, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume IV gas phase reactions of organic halogen species, *Atmos. Chem. Phys.*, *9*, 4141-4496, 2008.

Table 3.1. Reaction-rate coefficients and estimated uncertainties for the OH + 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	–	*10*	*9695*	*<1 (-25)*	–	–	1,2
2. CFC-12	CCl_2F_2	–	*10*	*11910*	*<1 (-28)*	–	–	1,2
3. CFC-113	CCl_2FCClF_2	–	*10*	*>6220*	*<1 (-20)*	–	–	3,4
4. CFC-114	$CClF_2CClF_2$	–	*10*	*>6220*	<1 (-20)	–	–	3,4
5. CFC-115	CF_3CClF_2	–	*10*	*>6220*	*<1 (-20)*	–	–	3,4
6. Carbon Tetrachloride	CCl_4	–	*10*	*6220*	*<1 (-20)*	–	–	1,2
7. Nitrous oxide	N_2O	–	–	–	*<5.0 (-17)*	–	–	3,a
8. Halon-1202	CBr_2F_2	–	*1*	*>2200*	*<5 (-16)*	–	–	5
9. Halon-1211	$CBrClF_2$	–	*1*	*>3500*	*<8 (-18)*	–	–	2,b
10. Halon-1301	$CBrF_3$	–	*1*	*>3600*	*<6 (-18)*	–	–	5
11. Halon-2402	$CBrF_2CBrF_2$	–	*1*	*>3600*	*<6 (-18)*	–	–	5
12. Methane	CH_4	195 – 300	1.85	1690	6.4 (-15)	1.05	50	2,c
13. Methyl Chloroform	CH_3CCl_3	233 – 379	1.64	1520	1.0 (-14)	1.10	50	5,6
14. Methyl Chloride	CH_3Cl	224 – 298	1.96	1200	3.5 (-14)	1.10	50	2,6,d
15. Methyl Bromide	CH_3Br	233 – 300	1.40	1150	3.0 (-14)	1.07	100	2,6,e
16. HCFC-22	$CHClF_2$	250 – 391	1.03	1600	4.8 (-15)	1.07	100	2,6
17. HCFC-141b	CH_3CCl_2F	250 – 400	1.25	1600	5.8 (-15)	1.07	100	5,6,f
18. HCFC-142b	CH_3CClF_2	223 – 400	1.30	1770	3.4 (-15)	1.15	50	5,6
19. HFC-23	CHF_3	252 – 298	0.52	2210	3.1 (-16)	1.15	100	5
20. HFC-32	CH_2F_2	222 – 384	1.70	1500	1.1 (-14)	1.07	100	5,6
21. HFC-125	CHF_2CF_3	220 – 364	0.60	1700	2.0 (-15)	1.10	100	5,6,g
22. HFC-134a	CH_2FCF_3	223 – 400	0.95	1600	4.4 (-15)	1.10	100	2,6,h
23. HFC-143a	CF_3CH_3	261 – 403	1.06	2010	1.25 (-15)	1.10	100	2,i
24. HFC-152a	CH_3CHF_2	210 – 300	0.87	975	3.3 (-14)	1.05	50	5,6,j
25. HFC-227ea	CF_3CHFCF_3	250 – 400	0.48	1680	1.7 (-15)	1.15	75	2,6,k
26. HFC-245fa	$CHF_2CH_2CF_3$	273 – 370	0.61	1330	7.0 (-15)	1.15	100	5,6
27. Nitrogen Trifluoride	NF_3	–	*10*	*>17500*	*<3 (-37)*	–	–	1,3,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 The recommendation given here was obtained by setting the pre-exponential factor (*A*) to 1×10^{-11} 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. The JPL10-6 recommendation was derived from experimentally determined rate-coefficient upper limits.

2 *A* and/or *E*/R recommendation is revised from JPL10-6.

3 Not evaluated in JPL10-6.

4 The recommended kinetic parameters are taken to be equal to those for the OH + CCl_4 reaction.

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

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

a Based on the study by Biermann *et al.* (1976), who measured a rate coefficient of 3.8 $\times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. A more conservative upper limit (4.0×10^{-16} cm^3 $molecule^{-1}$ s^{-1}) was reported by Chang and Kaufman (1977b).

b Rate-coefficient expression was estimated using an estimated Arrhenius *A*-factor and the rate-coefficient upper limit reported by Burkholder *et al.* (1991) at 373 K.

c *A* and/or *E*/R recommendation was taken from IUPAC data evaluation.

d The recommended *k*(298 K) was obtained from an average of the data of Hsu and DeMore (1994), Orkin *et al.* (2013), and Herndon *et al.* (2001). The recommended *E*/R was obtained from a fit to the data of Herndon *et al.* below 298 K.

e The recommended *k*(298 K) was obtained from an average of the data of Hsu and DeMore (1994) (recalculated based on the JPL10-6-recommended rate coefficient for the OH + CH_3CHF_2 reference reaction), Chichinin *et al.* (1994), Mellouki *et al.* (1992), and Zhang *et al.* (1992). The recommended value for *E*/R was derived from a fit to the data of Mellouki *et al.* below 300 K.

f The data from Lancar *et al.* (1993) at T<400 K were used in the fit to obtain E/R.

g The recommended *k*(298 K) was obtained from an average of the data of Talukdar *et al.* (1991), DeMore (1993), and Young *et al.* (2009). The recommended value for *E*/R was taken from Talukdar *et al.*

h The present analysis differs from that given in JPL10-6 in that the three rate coefficients reported in DeMore (1993) were averaged in the determination of *E*/R.

i The present analysis differs from that given in JPL10-6 in that the DF-LMR results of Talukdar *et al.* (1991) were not included in the analysis for *k*(298 K), although their LP-LIF results were included.

j The site-specific rate coefficients were estimated by Kozlov *et al.* (2003) to be 33% reaction at the CH_3 group and 67% H atom abstraction from the CH_2F group.

k The recommended k(298 K) was obtained from an average of the results from the absolute-rate studies of Nelson *et al.* (1993), Zellner *et al.* (1994), Zhang *et al.* (1994), and Tokuhashi *et al.* (2004) and the relative rate studies of Hsu and DeMore (1995) (recalculated based on the JPL10-6-recommended rate coefficients for the OH + CH_4 and OH + CHF_2CF_3 reference reactions) and Wallington *et al.* (2004) (recalculated based on the JPL10-6-recommended rate coefficient for the OH + C_2H_4 and OH + C_2H_2 reference reactions). The recommended value for E/R was based on a fit of the data below 400 K from Nelson *et al.* (1993), Zellner *et al.* (1994), Tokuhashi *et al.* (2004), and Hsu and DeMore (1995) after scaling to the recommended k(298 K) value.

l The rate-coefficient parameters were estimated using a G3B3 quantum chemical method (Curtiss *et al.*, 2001) calculation of the reaction activation barrier, ~146 kJ mol^{-1}. Assuming a pre-exponential factor of 1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and E/R equal to the calculated activation barrier provides the basis of the recommendation.

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Zhang, Z., R. D. Saini, M. J. Kurylo, and R. E. Huie, A temperature dependent kinetic study of the reaction of the hydroxyl radical with CH_3Br, *Geophys. Res. Lett.*, *19*, 2413-2416, 1992.

1. $CFCl_3$ (CFC-11)

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-11} \exp(-9695/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 1 \times 10^{-25}$ cm^3 molecule^{-1} s^{-1}

Recommendations were revised from JPL10-6.[1]

The current recommendation was obtained by equating the activation energy (E) to the endothermicity for the abstraction of a Cl atom following IUPAC (Atkinson *et al.,* 2008) and setting the pre-exponential factor (A) to 1×10^{-11} cm^3 molecule^{-1} s^{-1}. The JPL10-6 recommendation was derived from typically less-sensitive rate-coefficient upper limits estimated from instrumental sensitivity towards reaction rate measurements.

2. CF_2Cl_2 (CFC-12)

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-11} \exp(-11910/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 1 \times 10^{-28}$ cm^3 molecule^{-1} s^{-1}

Recommendations were revised from JPL10-6.[1]

The current recommendation was obtained by equating the activation energy (E) to the endothermicity for the abstraction of a Cl atom following IUPAC (Atkinson *et al.,* 2008) and setting the pre-exponential factor (A) to 1×10^{-11} cm^3 molecule^{-1} s^{-1}. The JPL10-6 recommendation was derived from typically less-sensitive rate-coefficient upper limits estimated from instrumental sensitivity towards reaction rate measurements.

3. $CF_2ClCFCl_2$ (CFC-113)

Recommended Rate Coefficient

$k(T) = 1 \times 10^{-11} \exp(-6220/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) = 1 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}

Not evaluated in JPL10-6[1] or IUPAC.[2]

The recommended kinetic parameters are taken to be equal to those estimated for the OH + CCl_4 reaction.

4. CF_2ClCF_2Cl (CFC-114)

Recommended Rate Coefficient
$k(T) < 1 \times 10^{-11} \exp(-6220/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 1 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}

Not evaluated in JPL10-6[1] or IUPAC.[2]

The recommended kinetic parameters are taken to be equal to those estimated for the OH + CCl_4 reaction.

5. CF_3CF_2Cl (CFC-115)

Recommended Rate Coefficient
$k(T) = 1 \times 10^{-11} \exp(-6220/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) = 1 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}

Not evaluated in JPL10-6[1] or IUPAC[2].

The recommended kinetic parameters are taken to be equal to those estimated for the OH + CCl_4 reaction.

6. CCl_4 (Carbon Tetrachloride)

Recommended Rate Coefficient
$k(T) < 1 \times 10^{-11} \exp(-6220/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\ K) < 1 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}

Recommendations were revised from JPL10-6.[1]

The current recommendation was obtained by equating the activation energy (*E*) to the endothermicity for the abstraction of a Cl atom following IUPAC and setting the pre-exponential factor (*A*) to 1×10^{-11} cm^3 molecule^{-1} s^{-1}. The JPL10-6 recommendation was derived from typically less-sensitive rate-coefficient upper limits estimated from instrumental sensitivity towards reaction-rate measurements.

7. N_2O

Recommended Rate Coefficient

$k(298\ K) < 5 \times 10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$

Not evaluated in JPL10-6.[1]

The current recommendation is based on the study by Biermann *et al.* (1976), who measured a rate constant of $3.8 \times 10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K. A more conservative upper limit ($4.0 \times 10^{-16}\ cm^3\ molecule^{-1}\ s^{-1}$) was reported by Chang and Kaufman (1977).

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8. CF_2Br_2 (Halon-1202)

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-12} \exp(-2200/T)\ cm^3\ molecule^{-1}\ s^{-1}$

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

Recommendations are unchanged from JPL10-6.[1]

The rate coefficient was estimated using an estimated Arrhenius *A*-factor and the rate-coefficient upper limit reported by Burkholder *et al.* (1991) at 298 K.

Reference

Burkholder, J. B., R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, Atmospheric fate of CF_3Br, CF_2Br_2, CF_2ClBr, and CF_2BrCF_2Br, *J. Geophys. Res.*, *96*, 5025-5043, 1991.

9. CF_2ClBr (Halon-1211)

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-12} \exp(-3500/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\text{ K}) < 8 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}

Recommendations were revised from JPL10-6.[1]

The rate coefficient was estimated using an estimated Arrhenius *A*-factor and the rate-coefficient upper limit reported by Burkholder *et al.* (1991) at 373 K.

Reference

Burkholder, J. B., R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, Atmospheric fate of CF_3Br, CF_2Br_2, CF_2ClBr, and CF_2BrCF_2Br, *J. Geophys. Res.*, *96*, 5025-5043, 1991.

10. CF_3Br (Halon-1301)

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-12} \exp(-3600/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\text{ K}) < 6 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}

Recommendations are unchanged from JPL10-6.[1]

The rate coefficient was estimated using an estimated Arrhenius *A*-factor and the rate-coefficient upper limit reported by Orkin and Khamaganov (1993) at 460 K.

Reference

Orkin, V. L., and V. G. Khamaganov, Rate constants for reactions of OH radicals with some Br-containing haloalkanes, *J. Atmos. Chem., 16,* 169-178, 1993.

11. CF_2BrCF_2Br (Halon-2402)

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-12} \exp(-3600/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\text{ K}) < 6 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}

Recommendations are unchanged from JPL10-6.[1]

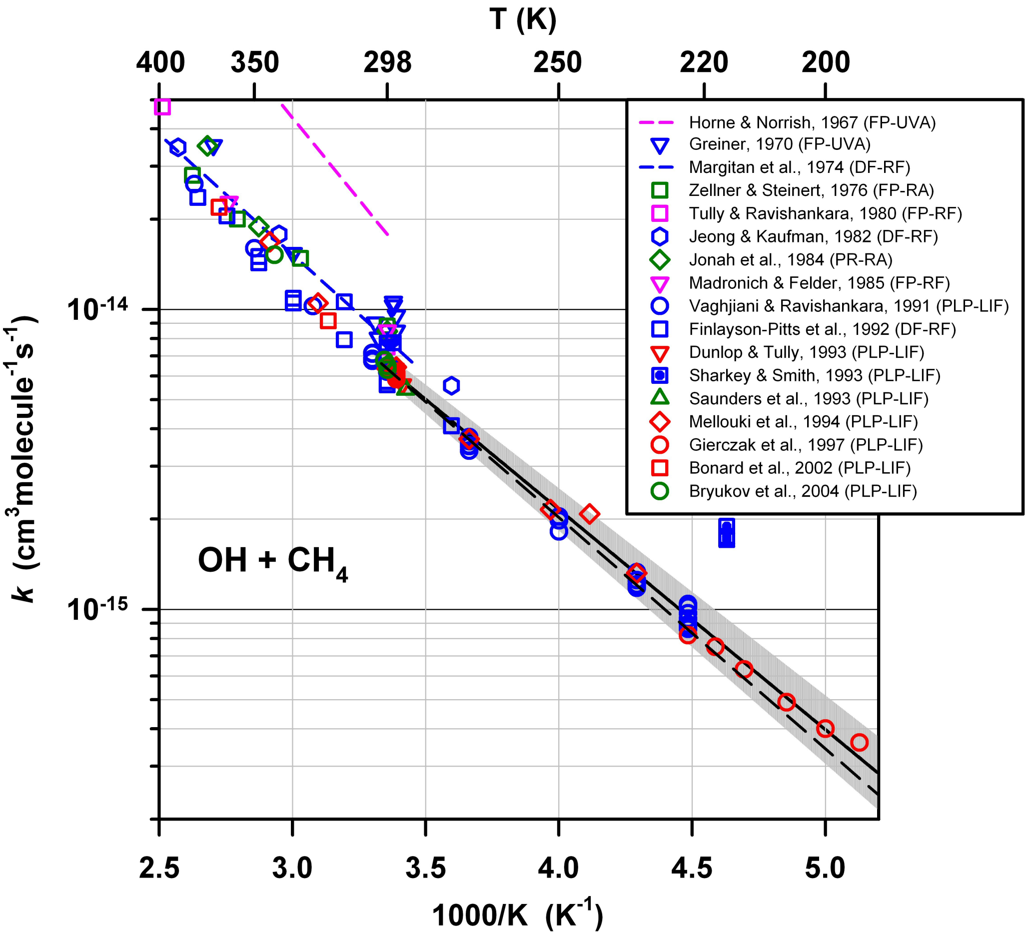
The rate coefficient was estimated using an estimated Arrhenius *A*-factor and the rate-coefficient upper limit reported by Orkin and Khamaganov (1993) at 460 K.

Reference

Orkin, V. L., and V. G. Khamaganov, Rate constants for reactions of OH radicals with some Br-containing haloalkanes, *J. Atmos. Chem., 16,* 169-178, 1993.

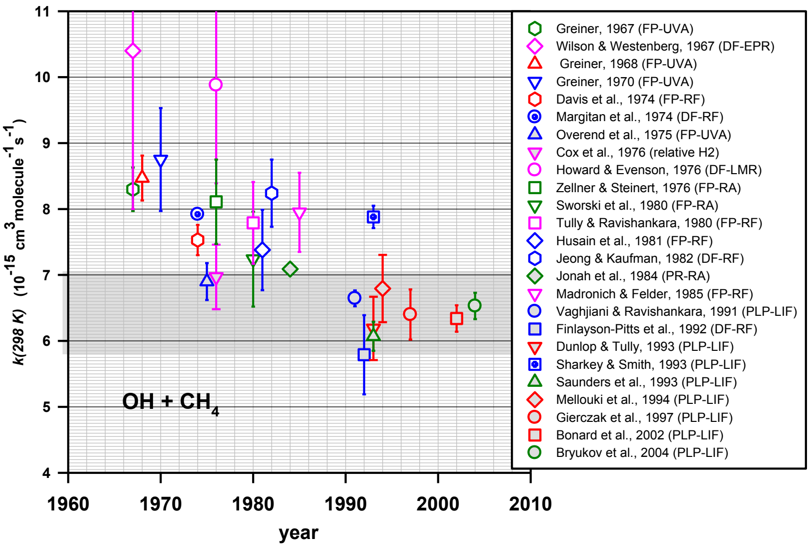
12. CH_4 (Methane)

Results of the temperature-dependence studies



The SPARC recommendation (solid line) over the temperature range 200 to 300 K was taken from the IUPAC data evaluation. The JPL10-6 recommendation (black dashed line) is lower by 15% at 200 K, 3% at 272 K, and 0.4% at 298 K is included for comparison.

History of *k*(298 K) measurements



The *k*(298 K) values are from the Arrhenius fits obtained from the studies of temperature dependences. The results obtained only at room temperature, near 298 K, were corrected slightly to obtain *k*(298 K) using the recommended *E*/R. The more recent studies are believed to be free from the influence of secondary reactions involving OH.

Recommended Rate Coefficient	**Recommended Uncertainty Factors**
$k(T) = 1.85\times 10^{-12} \exp(-1690/T)$ cm^3 molecule^{-1} s^{-1}	$f(298\text{ K}) = 1.05$
$k(298\text{ K}) = 6.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}	$g = 50$

A and *E*/R recommendations are unchanged from IUPAC.

f(298 K) and *g* were revised.

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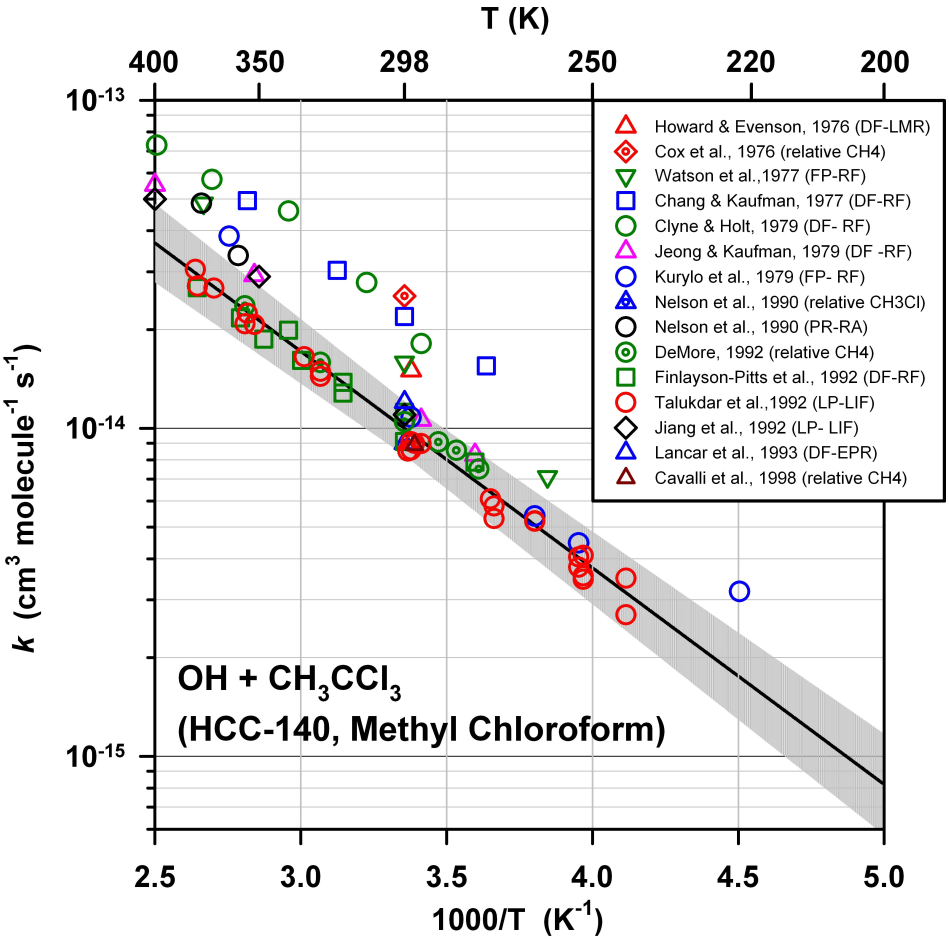
13. CH_3CCl_3 (Methyl Chloroform)



Recommended Rate Coefficient	**Recommended Uncertainty Factors**
$k(T) = 1.64 \times 10^{-12} \exp(-1520/T)$ cm^3 molecule^{-1} s^{-1}	$f(298\text{ K}) = 1.1$
$k(298\text{ K}) = 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}	$g = 50$

A and *E*/R recommendations are unchanged from JPL10-6.[1]

f(298 K) and *g* were revised from JPL10-6.[1]

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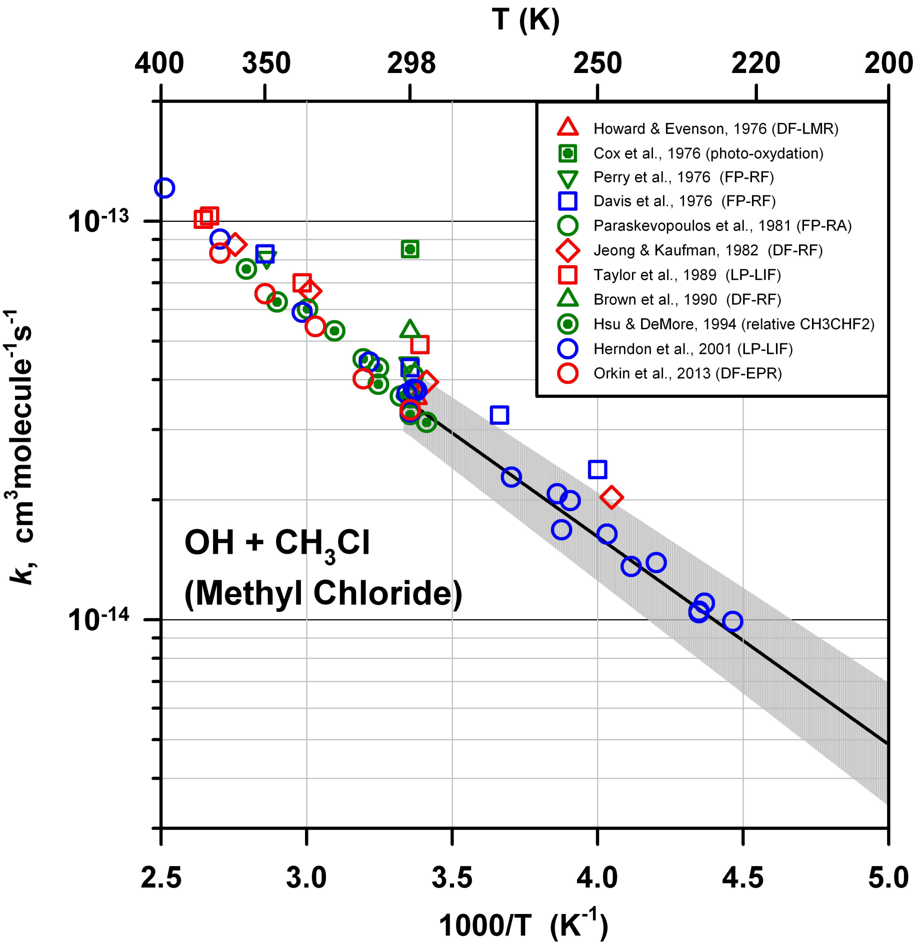
14. CH_3Cl (Methyl Chloride)



Recommended Rate Coefficient

$k(T) = 1.96 \times 10^{-12} \exp(-1200/T)$ cm^3 $molecule^{-1}$ s^{-1}

$k(298\ K) = 3.5 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

Recommended Uncertainty Factors

$f(298\ K) = 1.1$

$g = 50$

k(298 K) is an average of room temperature data of Hsu and DeMore, Orkin *et al.* (1994), and Herndon *et al.* (2001)

E/R from Herndon *et al.* (2001), below room temperature

f(298 K) and g were revised from JPL10-6.[1]

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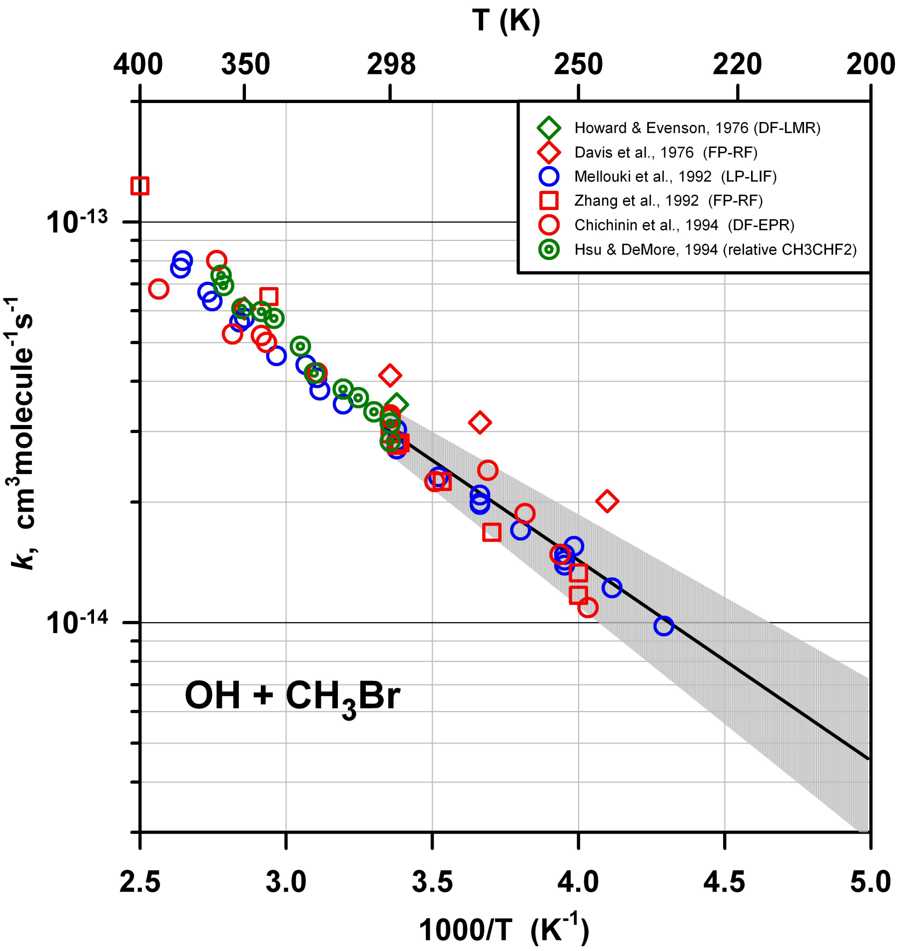
15. CH_3Br (Methyl Bromide)



Recommended Rate Coefficient:

$k(T) = 1.4 \times 10^{-12} \exp(-1150/T)$ cm^3 $molecule^{-1}$ s^{-1}

$k(298\ K) = 3.0 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

Recommended Uncertainty Factors

$f(298\ K) = 1.07$

$g = 100$

k(298 K) is an average of room temperature data of Mellouki *et al.* (1992), Zhang *et al.* (1992), Chichinin *et al.* (1994), and Hsu and DeMore (1994)

E/R from fit to Mellouki *et al.* (1992) below 300 K

f(298 K) was revised from JPL10-6;[1]

g is unchanged from JPL10-6.[1]

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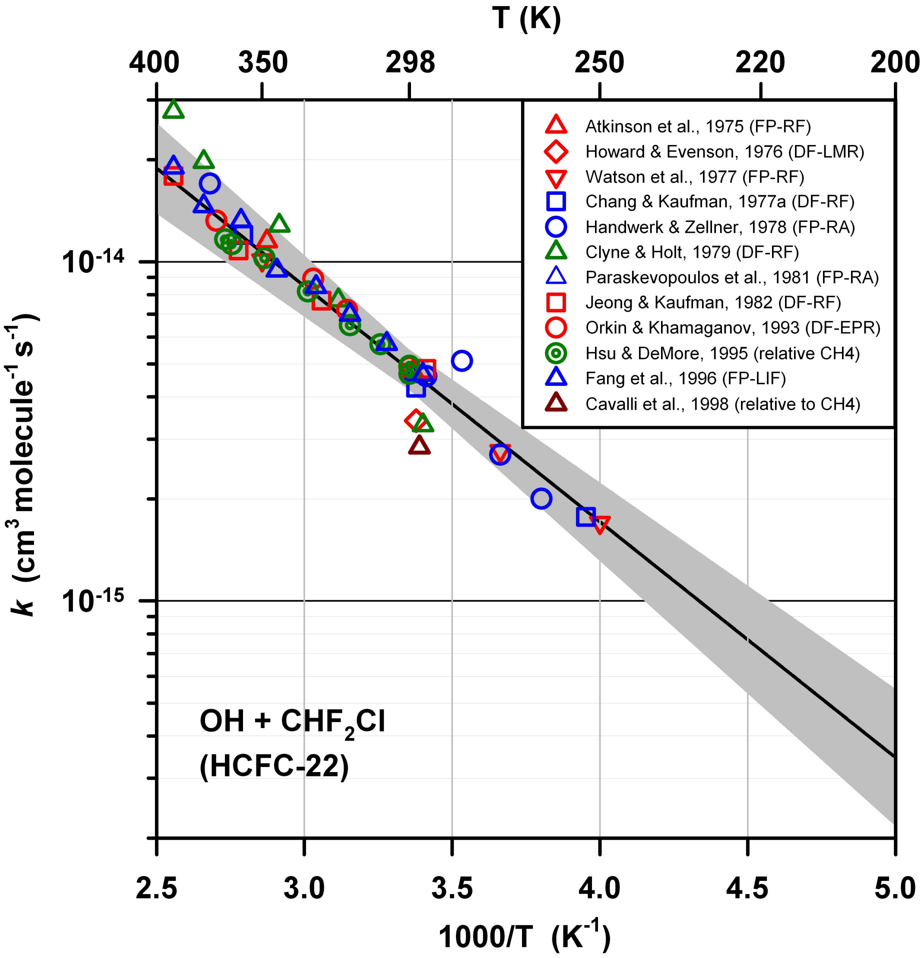
16. CHF_2Cl (HCFC-22)



Recommended Rate Coefficient

$k(T) = 1.03 \times 10^{-12} \exp(-1600/T)$ cm^3 molecule^{-1} s^{-1}

$k(298\ K) = 4.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298\ K) = 1.07$

$g = 100$

A recommendation changed and *E*/R recommendations are unchanged from JPL10-6.[1]

f(298 K) and *g* were revised from JPL10-6.[1]

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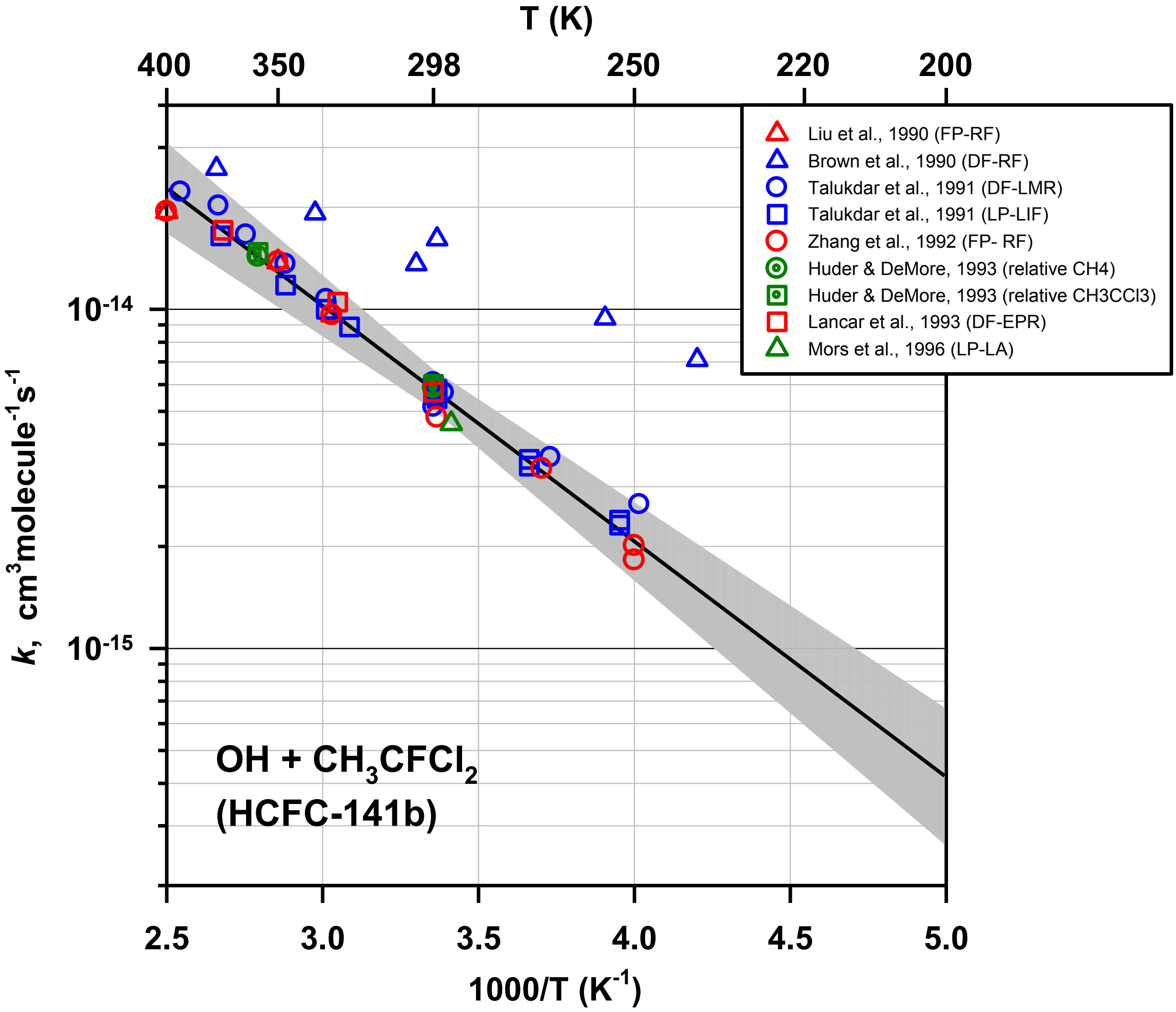
17. CH_3CFCl_2 (HCFC-141b)



Recommended Rate Coefficient

$k(T) = 1.25 \times 10^{-12} \exp(-1600/T)$ cm^3 $molecule^{-1}$ s^{-1}
$k(298\ K) = 5.8 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

Recommended Uncertainty Factors

$f(298\ K) = 1.07$
$g = 100$

A and *E*/R recommendations are unchanged from JPL10-6.[1]

f(298 K) and *g* were revised from JPL10-6.[1]

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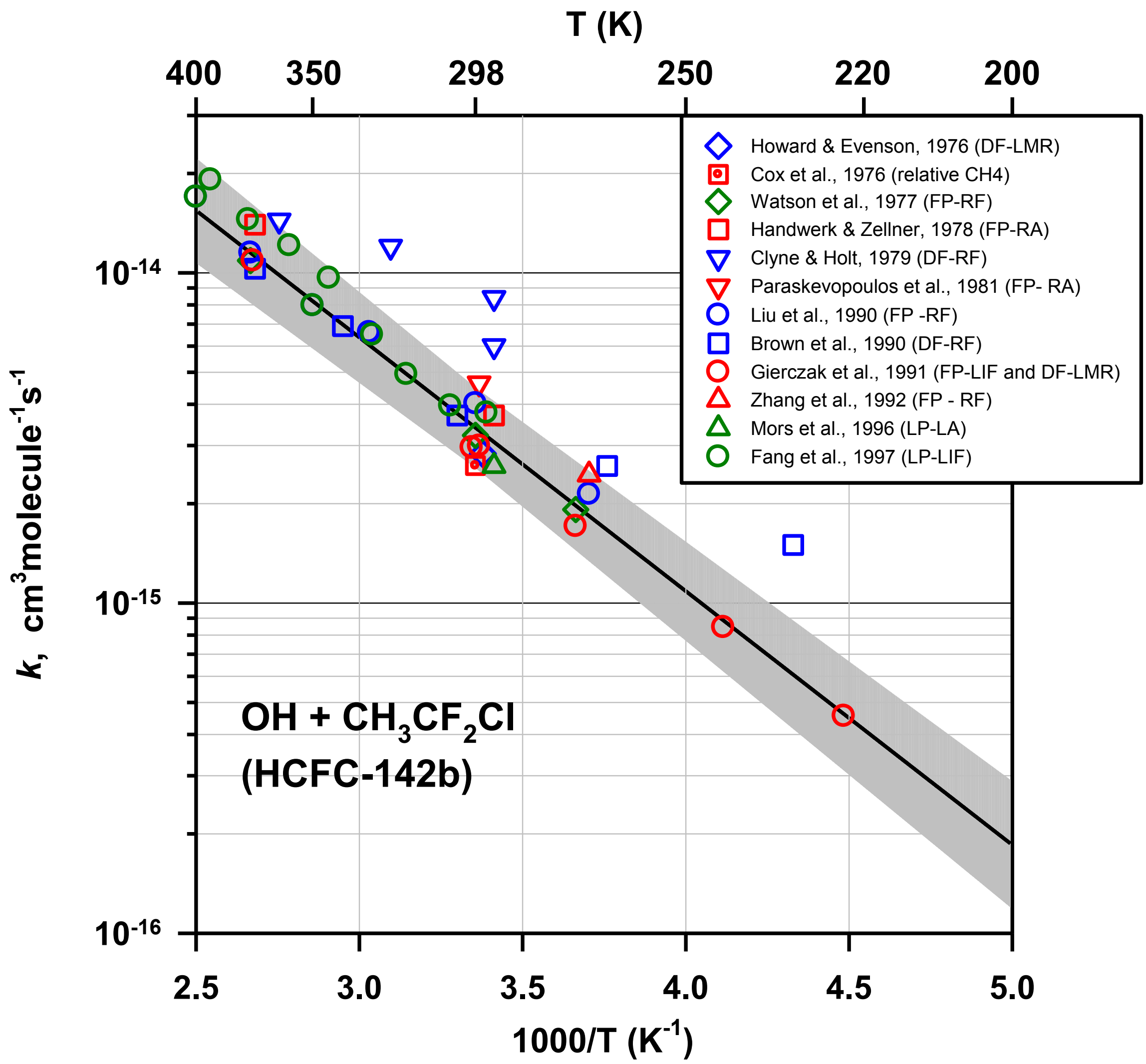
18. CH_3CF_2Cl (HCFC-142b)



Recommended Rate Coefficient

$k(T) = 1.30 \times 10^{-12} \exp(-1770/T)$ cm^3 molecule^{-1} s^{-1}
$k(298 \text{ K}) = 3.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298 \text{ K}) = 1.15$
$g = 50$

A and *E*/R recommendations are unchanged from JPL10-6.[1]

f(298 K) and g were revised from JPL10-6.[1]

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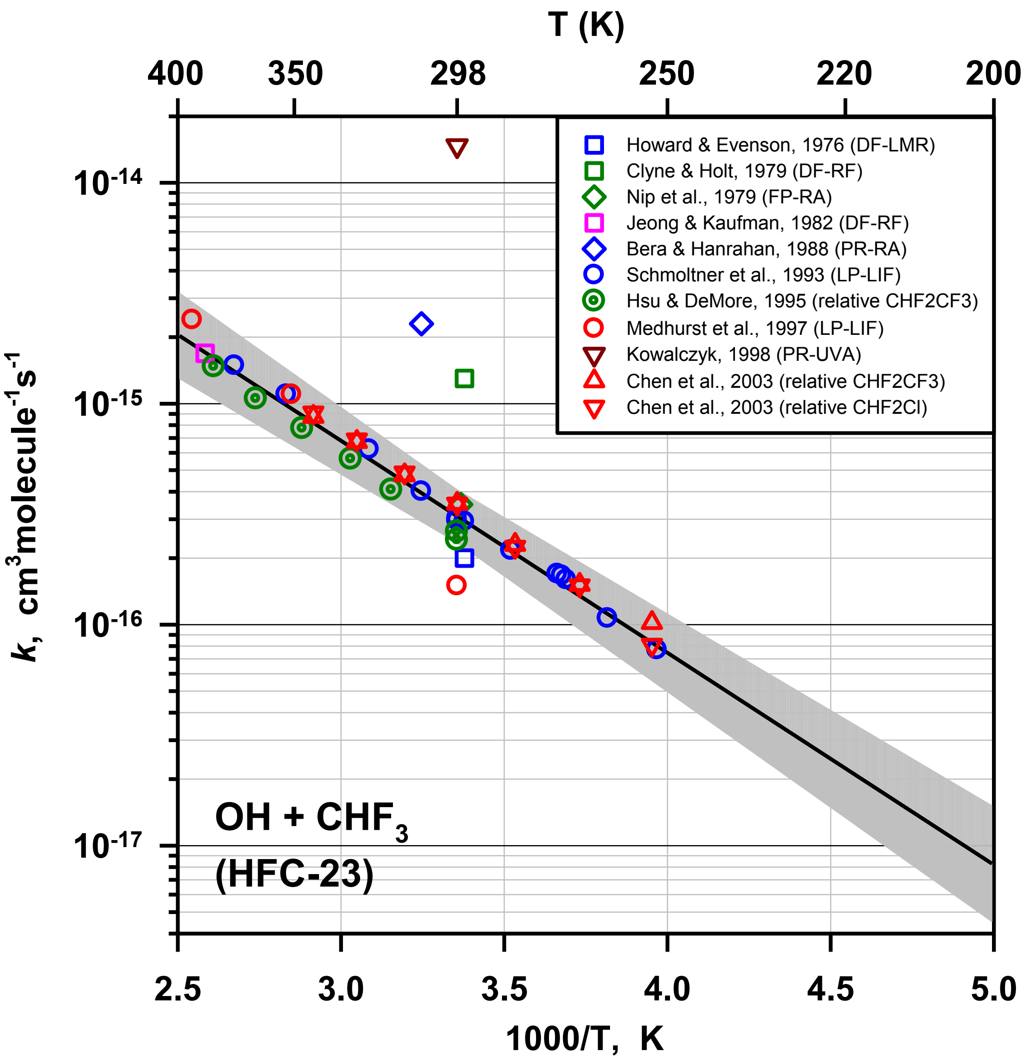
19. CHF_3 (HFC-23)



Recommended Rate Coefficient

$k(T) = 0.52 \times 10^{-12} \exp(-2210/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\text{ K}) = 3.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298\text{ K}) = 1.15$
$g = 100$

A and *E*/R recommendations are unchanged from JPL10-6.[1]

f(298 K) and *g* are unchanged from JPL10-6.[1]

References

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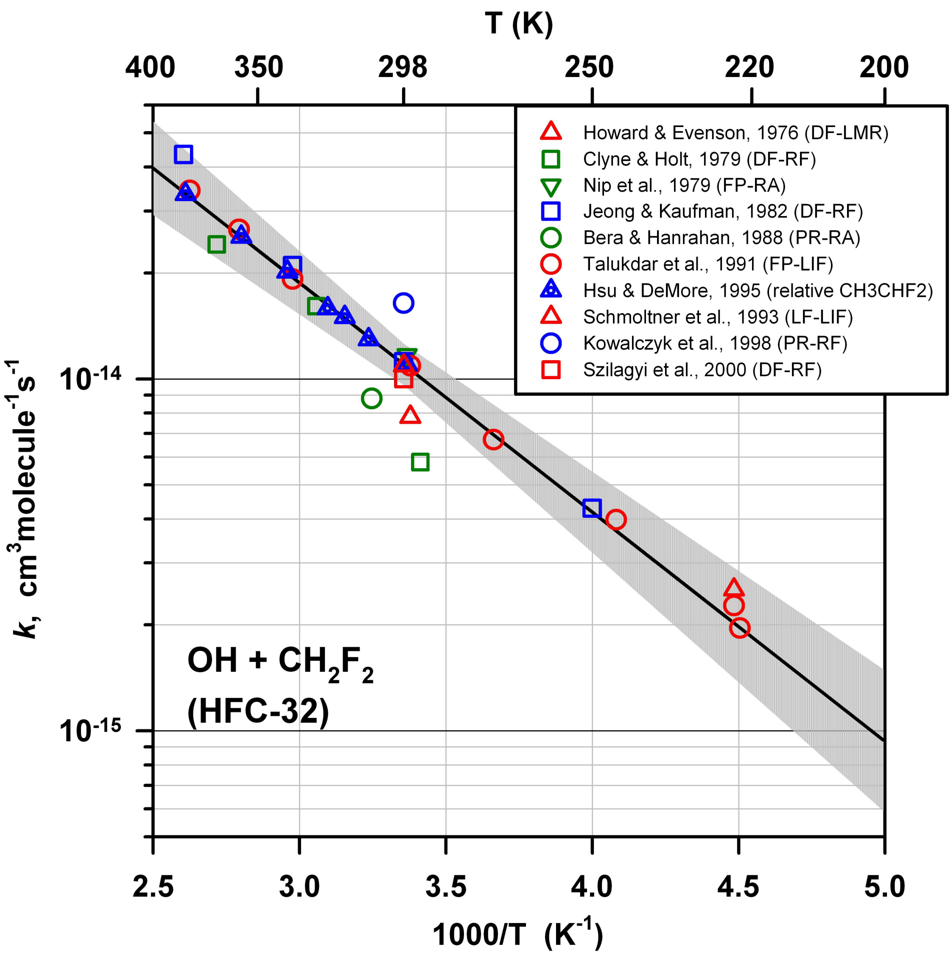
20. CH_2F_2 (HFC-32)



Recommended Rate Coefficient

$k(\mathrm{T}) = 1.7 \times 10^{-12} \exp(-1500/\mathrm{T})\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$

$k(298\ \mathrm{K}) = 1.1 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$

Recommended Uncertainty Factors

$f(298\ \mathrm{K}) = 1.07$

$g = 100$

A and *E*/R recommendations are unchanged from JPL10-6.[1]

f(298 K) and g were revised from JPL10-6.[1]

References

Bera, R. K., and R. J. Hanrahan, Investigation of gas-phase reactions of OH radicals with fluoromethane and difluoromethane using Ar-sensitized pulse-radiolysis, *Rad. Phys. Chem.*, *32*, 579-584, 1988.

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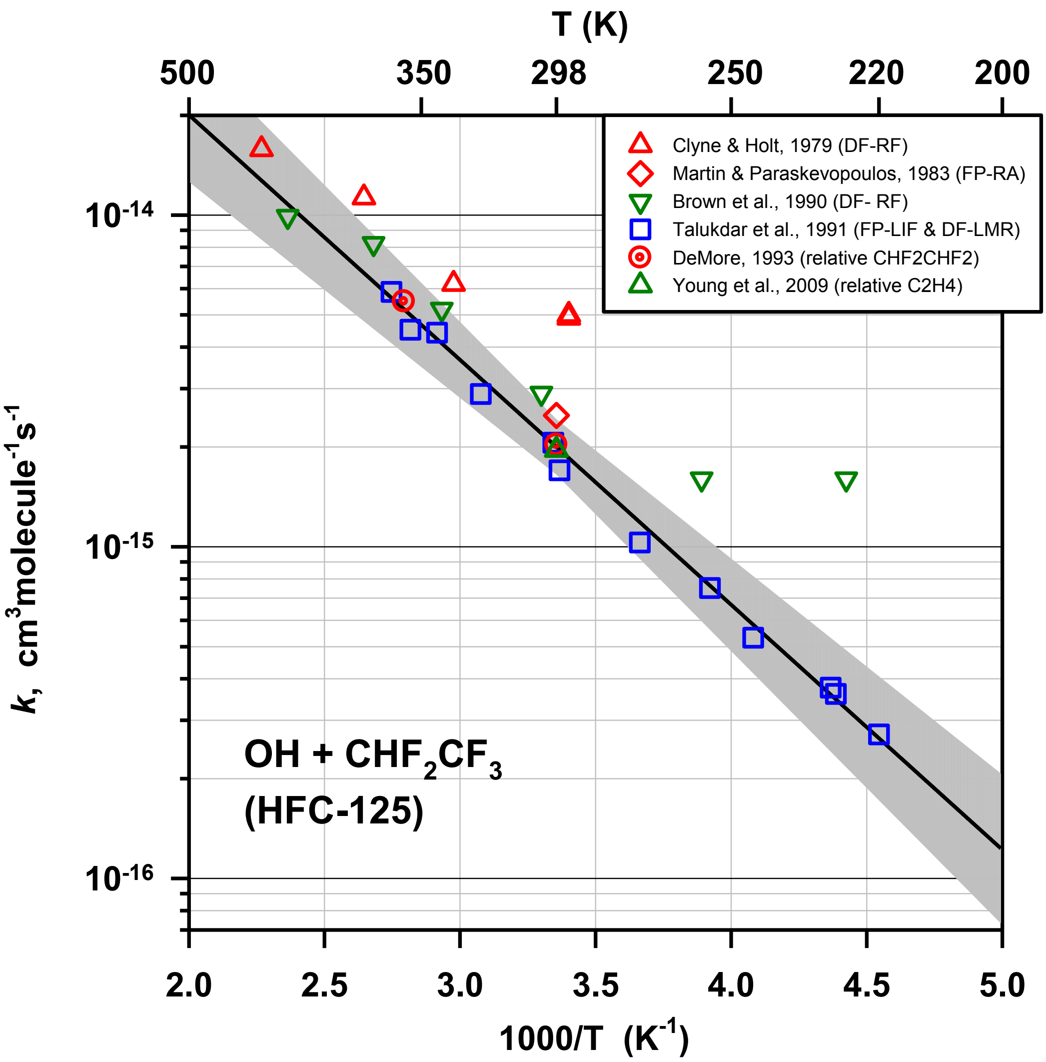
21. CHF_2CF_3 (HFC-125)



Recommended Rate Coefficient

$k(T) = 0.60 \times 10^{-12} \exp(-1700/T)$ cm^3 molecule^{-1} s^{-1}
$k(298\text{ K}) = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298\text{ K}) = 1.1$
$g = 100$

A and *E*/R recommendations are unchanged from JPL10-6.[1]

f(298 K) and *g* were revised from JPL10-6.[1]

References

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Clyne, M. A. A., and P. M. Holt, Reaction kinetics involving ground $X^2\Pi$ and excited $A^2\Sigma^+$ hydroxyl radicals. Part 2. Rate constants for reactions of OH $X^2\Pi$ with halogenomethanes and halogenoethanes, *J. Chem. Soc. Faraday Trans., 2*, *75*, 582-591, 1979.

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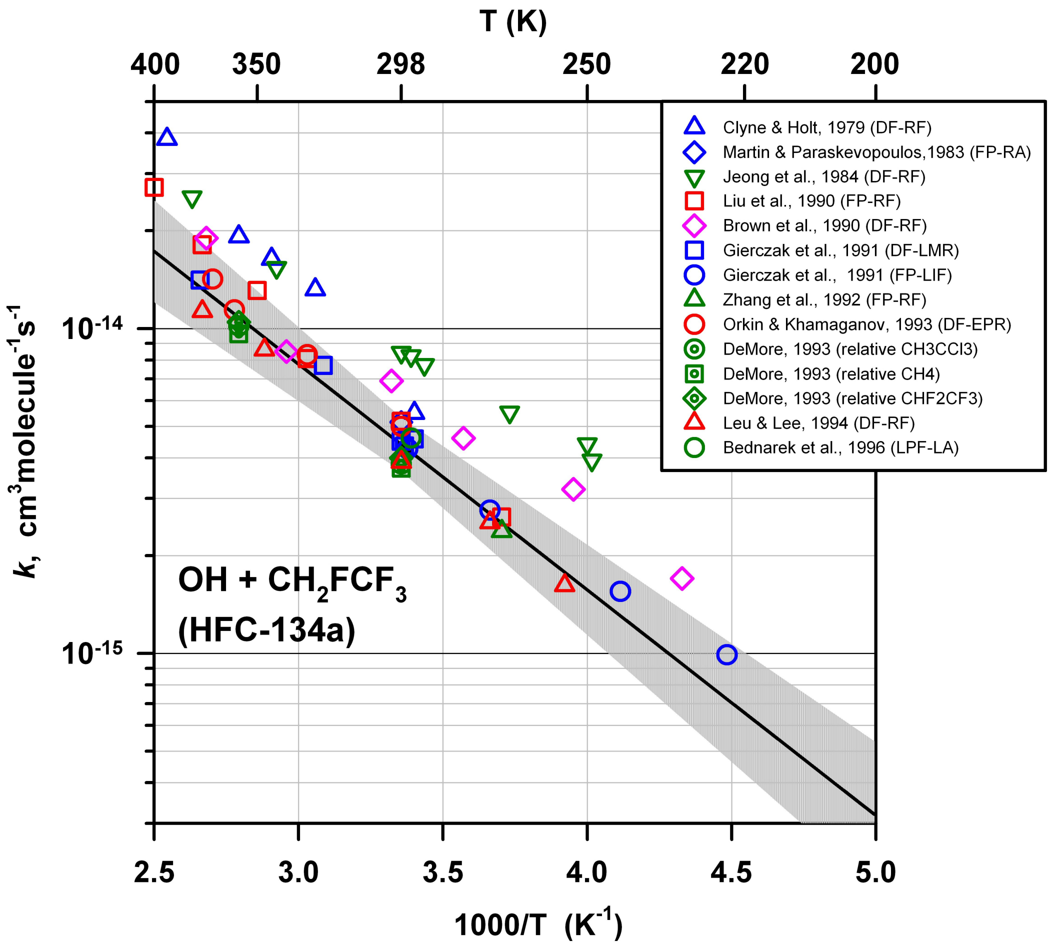
22. CH_2FCF_3 (HFC-134a)



Recommended Rate Coefficient

$k(\mathrm{T}) = 0.95 \times 10^{-12} \exp(-1600/\mathrm{T})$ cm^3 molecule^{-1} s^{-1}
$k(298\ \mathrm{K}) = 4.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

$f(298\ \mathrm{K}) = 1.1$
$g = 100$

E/R is an average of E/R (T < 400 K) from Liu *et al.* (1990), Gierczak *et al.* (1991) (2 studies), Orkin and Khamaganov (1993), Leu and Lee (1994), and DeMore (1993) (3 studies were averaged to give a single E/R).

f(298 K) is unchanged from JPL10-6;[1]

g was revised from JPL10-6.[1]

References

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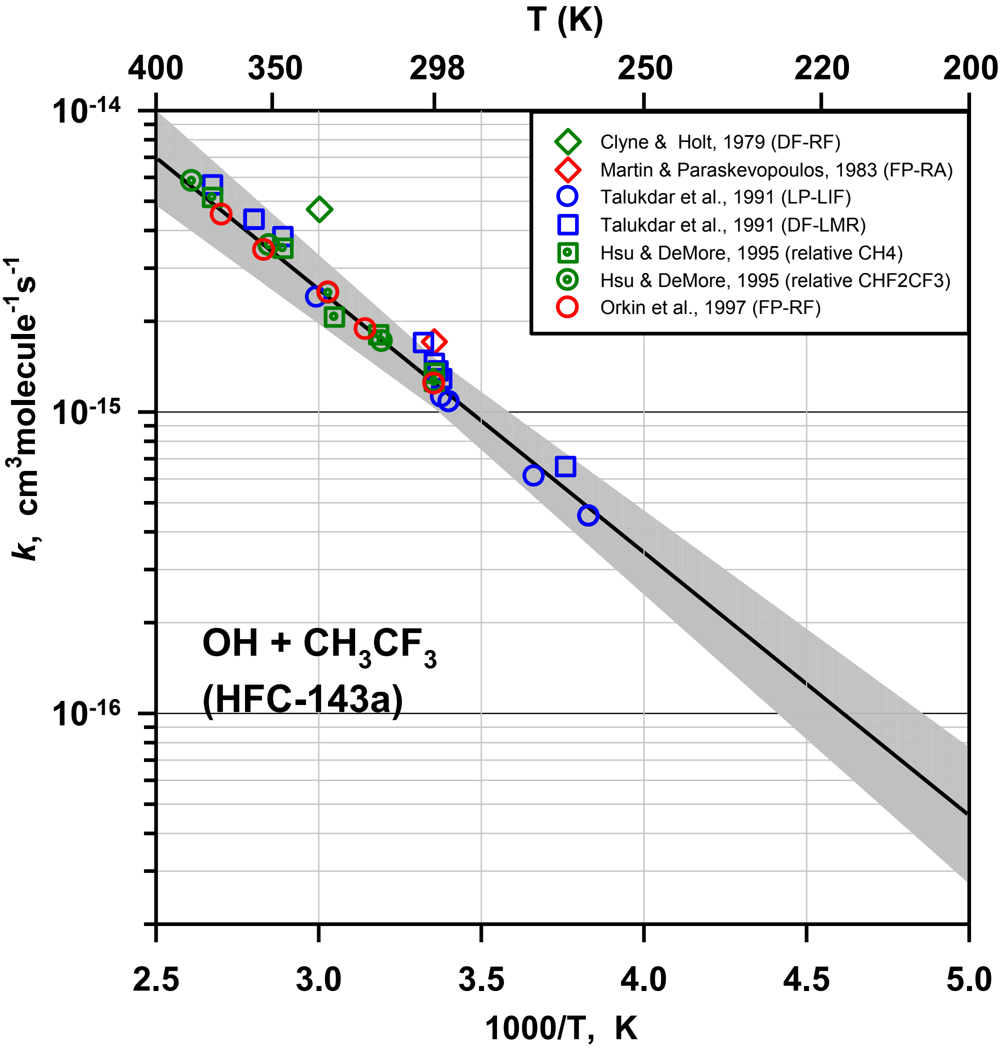
23. CH_3CF_3 (HFC-143a)



Recommended Rate Coefficient

k(T) = 1.06 × 10^{-12} exp(-2010/T) cm^3 molecule^{-1} s^{-1}
k(298 K) = 1.25 × 10^{-15} cm^3 molecule^{-1} s^{-1}

Recommended Uncertainty Factors

f(298 K) = 1.1
g = 100

Recommended k(298 K) is an average of room temperature data from Talukdar *et al.* (1991), (LP-LIF), Hsu and DeMore (1995) (2 studies), and Orkin *et al.* (1996). The Talukdar *et al.* (DF-LMR) data appear to be systematically high.

Recommended E/R is an average of values from Talukdar *et al.* (2 values), Hsu and DeMore (2 values), and Orkin *et al.*

f(298 K) and g are unchanged from JPL10-6.[1]

References

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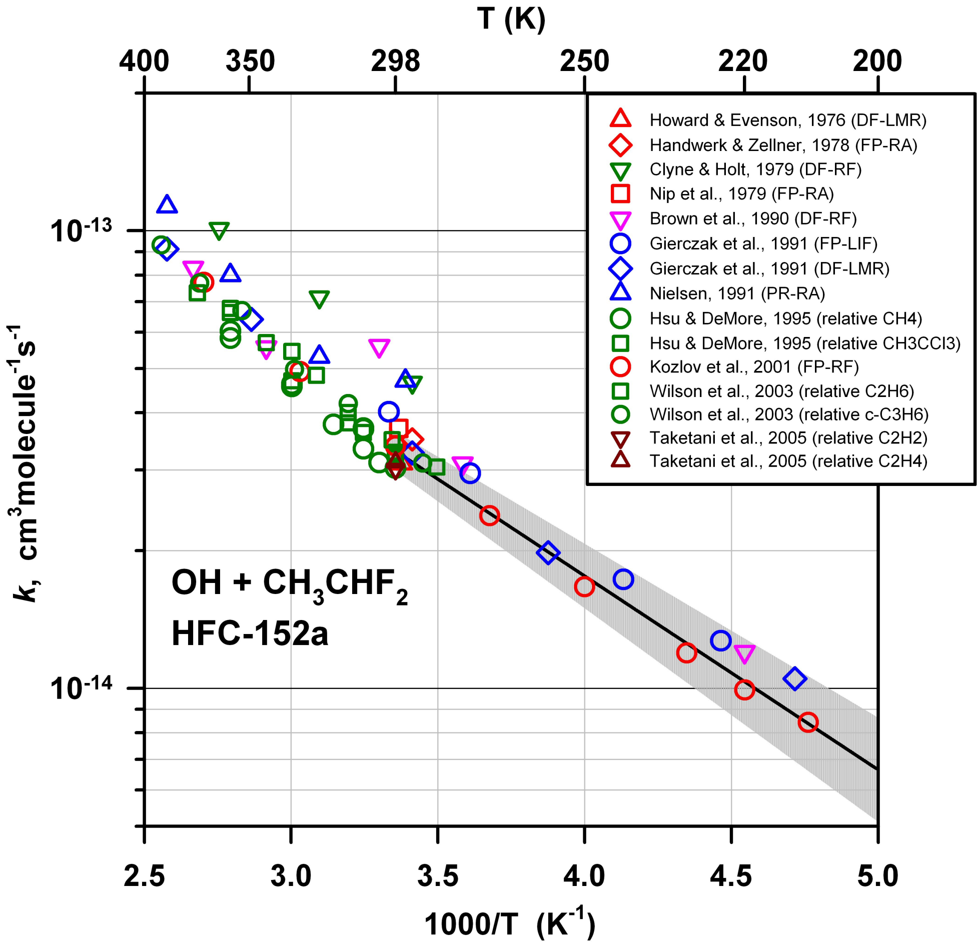
24. CH_3CHF_2 (HFC-152a)



Recommended Rate Coefficient

$k(T) = 0.87 \times 10^{-12} \exp(-975/T)$ cm^3 $molecule^{-1}$ s^{-1}
$k(298\ K) = 3.3 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

Recommended Uncertainty Factors

$f(298\ K) = 1.05$
$g = 50$

A and E/R recommendations are unchanged from JPL10-6.[1]

$f(298\ K)$ was revised from JPL10-6;[1] g is unchanged from JPL10-6.[1]

References

Brown, A. C., C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Laboratory studies of some halogenated ethanes and ethers: Measurements of rates of reaction with OH and of infrared absorption cross-sections, *Atmos. Environ.*, *24A*, 2499-2511, 1990.

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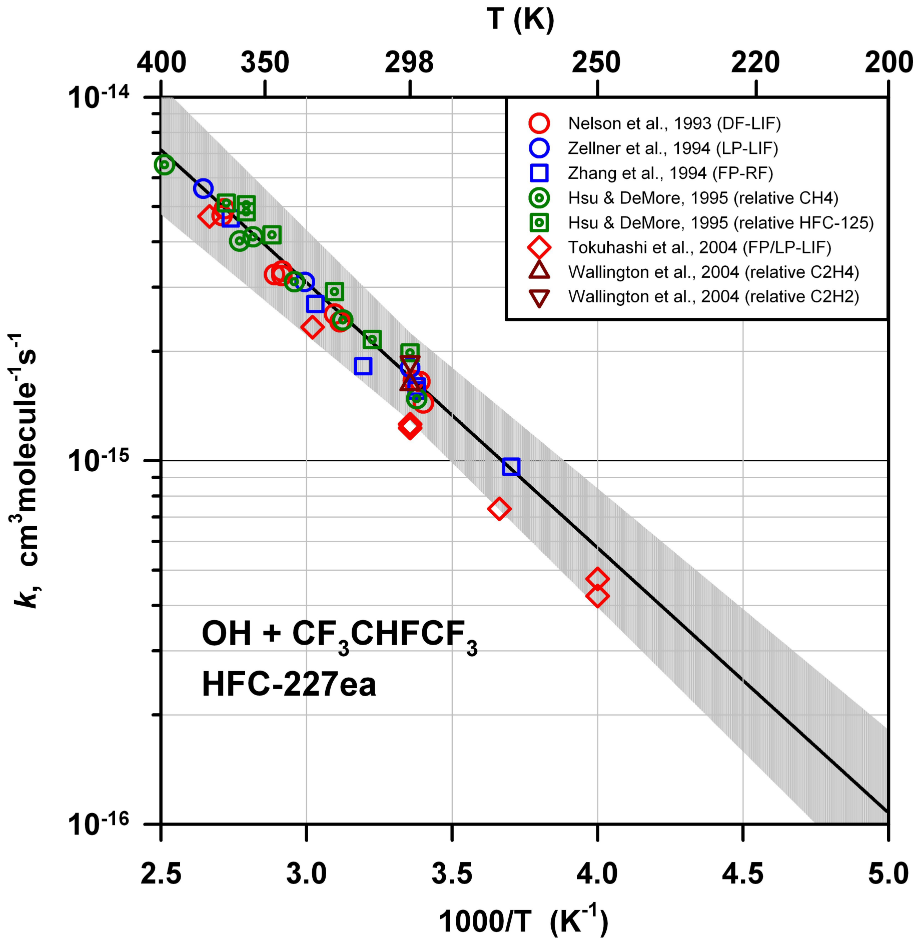
Wilson, E. W., A. M. Jacoby, S. J. Kukta, L. E. Gilbert, and W. B. DeMore, Rate constants for reaction of CH_2FCH_2F (HFC-152) and CH_3CHF_2 (HFC-152a) with hydroxyl radicals, *J. Phys. Chem. A*, *107*, 9357-9361, 2003.

25. CF_3CHFCF_3 (HFC-227ea)



Recommended Rate Coefficient

$k(T) = 0.48 \times 10^{-12} \exp(-1680/T)$ cm^3 $molecule^{-1}$ s^{-1}
$k(298\ K) = 1.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

Recommended Uncertainty Factors

$f(298\ K) = 1.15$
$g = 75$

k(298 K) is an average of all room temperature results

E/R is from fit to Nelson *et al.* (1993), Zellner *et al.* (1994), Hsu and DeMore (1995) (2 studies), and Tokuhashi *et al.* (2004) (normalized to k(298 K) at temperatures < 400 K.

f(298 K) is unchanged from JPL10-6;[1]

g was revised from JPL10-6.[1]

References

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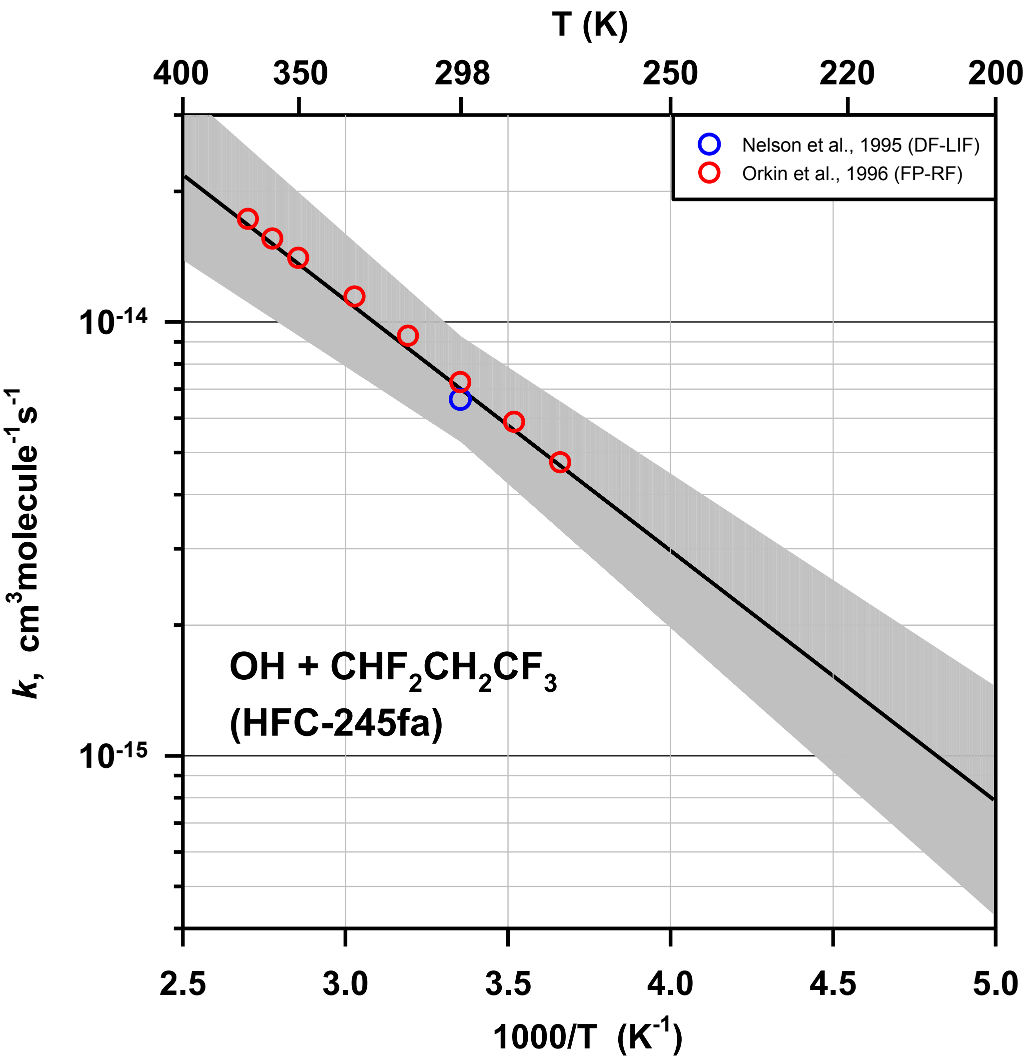
Zhang, Z., S. Padmaja, R. D. Saini, R. E. Huie, and M. J. Kurylo, Reactions of hydroxyl radicals with several hydrofluorocarbons: The temperature dependencies of the rate constants for $CHF_2CF_2CH_2F$ (HFC-245ca), $CF_3CHFCHF_2$ (HFC-236ea), CF_3CHFCF_3 (HFC-227ea), and $CF_3CH_2CH_2CF_3$ (HFC-356ffa), *J. Phys. Chem.*, *98*, 4312-4315, 1994.

26. $CHF_2CH_2CF_3$ (HFC-245fa)



Recommended Rate Coefficient

k(T) = 0.61 × 10^{-12} exp(-1330/T) cm^3 $molecule^{-1}$ s^{-1}

k(298 K) = 7.0 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1}

Recommended Uncertainty Factors

f(298 K) = 1.15

g = 100

A and E/R recommendations are unchanged from JPL10-6.[1]

f(298 K) and g were revised from JPL10-6.[1]

References

Nelson, D. D., M. S. Zahniser, C. E. Kolb, and H. Magid, OH reaction kinetics and atmospheric lifetime estimates for several hydrofluorocarbons, *J. Phys. Chem.*, *99*, 16301-16306, 1995.

Orkin, V. L., R. E. Huie, and M. J. Kurylo, Atmospheric lifetimes of HFC-143a and HFC-245fa, *J. Phys. Chem.*, *100*, 8907-8912, 1996.

27. NF_3

Recommended Rate Coefficient

$k(T) < 1 \times 10^{-11} \exp(-17500/T)$ cm^3 $molecule^{-1}$ s^{-1}
$k(298\ K) < 3 \times 10^{-37}$ cm^3 $molecule^{-1}$ s^{-1}

Not evaluated in JPL10-6.[1]

Dillon *et al.* (2011) reported a room temperature rate-coefficient upper limit of 4×10^{-16} cm^3 $molecule^{-1}$ s^{-1} for this reaction. F atom abstraction from NF_3 by the OH radical is endothermic by ~42 kJ mol^{-1} (Gurvich *et al.,* 1998; Karton *et al.,* 2009; Ruscic *et al.,* 2005). Equating the activation energy to this endothermicity and assuming a pre-exponential factor of 1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} yields a lower upper-limit rate coefficient of

$$k(T) < 1 \times 10^{-11} \exp(-5000/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k(298\ K) < 5 \times 10^{-19}\ cm^3\ molecule^{-1}\ s^{-1}$$

A G3B3 quantum chemical method (Curtiss *et al.,* 2001) calculation yields a similar reaction endothermicity (43 kJ mol^{-1}) and an activation barrier of ~146 kJ mol^{-1}. Assuming a pre-exponential factor of 1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} an even more restrictive upper-limit rate coefficient is obtained with this activation energy and provides the basis of the present recommendation

$$k(T) < 1 \times 10^{-11} \exp(-17500/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k(298\ K) < 3 \times 10^{-37}\ cm^3\ molecule^{-1}\ s^{-1}$$

References

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