IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx32

 The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 9, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.

This data sheet last evaluated: June 2015; last change in preferred values: June 2011.

$Cl + CH_2FCF_3$ (HFC-134a) $\rightarrow HCl + CHFCF_3$

$\Delta H° = 1.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.3) \times 10^{-15}$	297	Sawerysyn et al., 1992	DF-MS
$3.2 \times 10^{-12} \exp[-(2300 \pm 70)/T]$	298-423	Louis et al., 1997	DF-MS
$(1.4 \pm 0.3) \times 10^{-15}$	298		
Relative Rate Coefficients			
$(1.38 \pm 0.18) \times 10^{-15}$	295	Wallington and Hurley, 1992	RR (a)
$(1.6 \pm 0.3) \times 10^{-15}$	298	Tuazon et al., 1992	RR (a)
$2.1 \times 10^{-12} \exp(-1895/T)$	265-363	Kaiser, 1993	RR (b)
1.29×10^{-15}	296		
$1.27 \times 10^{-12} \exp(-2019/T)$	253-313	Nilsson et al., 2009	RR (c)
$(1.30 \pm 0.13) \times 10^{-15}$	298		

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio was placed on an absolute basis using $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(b) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant (CH_2FCF_3) and reference organic ($CHFClCF_3$) were measured by GC. The measured rate coefficient ratios was placed on an absolute basis using $k(Cl + CHFClCF_3) = 1.10 \times 10^{-12} \exp(-1800/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(c) Photolysis of Cl_2 in presence of Cl_2-CH_2FCF_3-CH_3CCl_3, Cl_2-CH_3CCl_3-CH_2F_2, and Cl_2-CH_2F_2-CH_4 mixtures in 930 mbar of N_2 diluent was used to measure the rate coefficient ratios $k(CH_2FCF_3)/k(CH_3CCl_3)$, $k(CH_3CCl_3)/k(CH_2F_2)$, and $k(CH_2F_2)/k(CH_4)$ at 253 – 313 K. Multiplication of the measured rate coefficients give values for $k(CH_2FCF_3)/k(CH_4)$. The values of $k(CH_2FCF_3)k(CH_4)$ obtained at < 300 K were placed on an absolute basis using $k(Cl+CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006). The value of $k(CH_2FCF_3)k(CH_4)$ obtained at 313 K was placed on an absolute basis using $k(Cl+CH_4) = 5.69 \times 10^{-19} T^{2.49} \exp(-609/T)$ cm^3 molecule^{-1} s^{-1} from Bryukov et al. (2002).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.4 x 10^{-15}	298
k /cm^3 molecule^{-1} s^{-1}	1.17 x 10^{-12} exp(-1996/T)	250-330
Reliability		
Δ log k	$\pm$ 0.06	298
$\Delta(E/R)$	$\pm$ 300	

Comments on Preferred Values

The results from Sawerysyn et al. (1992), Louis et al. (1997), Wallington and Hurley (1992) Tuazon et al. (1992), Kaiser (1993), and Nilsson et al. (2009) are in excellent agreement. The room temperature rate constant of Sawerysyn et al. (1992) is considered to be superseded by that measured in the same group by Louis et al. (1997). An average of the room temperature rate cofficients reported by Louis et al. (1997), Wallington and Hurley (1992) Tuazon et al. (1992), Kaiser (1993), and Nilsson et al. (2009) gives the recommended value at 298 K. The recommended Arrhenius expression is a fit to the data at T < 330 K from Louis et al. (1997), Wallington and Hurley (1992), Tuazon et al. (1992), Kaiser (1993), and Nilsson et al. (2009) with the A factor adjusted to give the recommended value at 298 K.

Fitting the three-parameter equation $k = CT^2 \exp(-D/T)$ to the data from by Louis et al. (1997), Wallington and Hurley (1992) Tuazon et al. (1992), Kaiser (1993), and Nilsson et al. (2009) gives k = 2.78 x 10^{-18} T^2 exp(-1530/T) cm^3 molecule^{-1} s^{-1} which can be used for temperatures above 330 K.

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr

Bryukov, M. G., Slagle, I. R., and Knyazev, V. D.: J. Phys. Chem. A, 106, 10532, 2002.

Kaiser, E. W.: Int. J. Chem. Kinet., 25, 667, 1993.

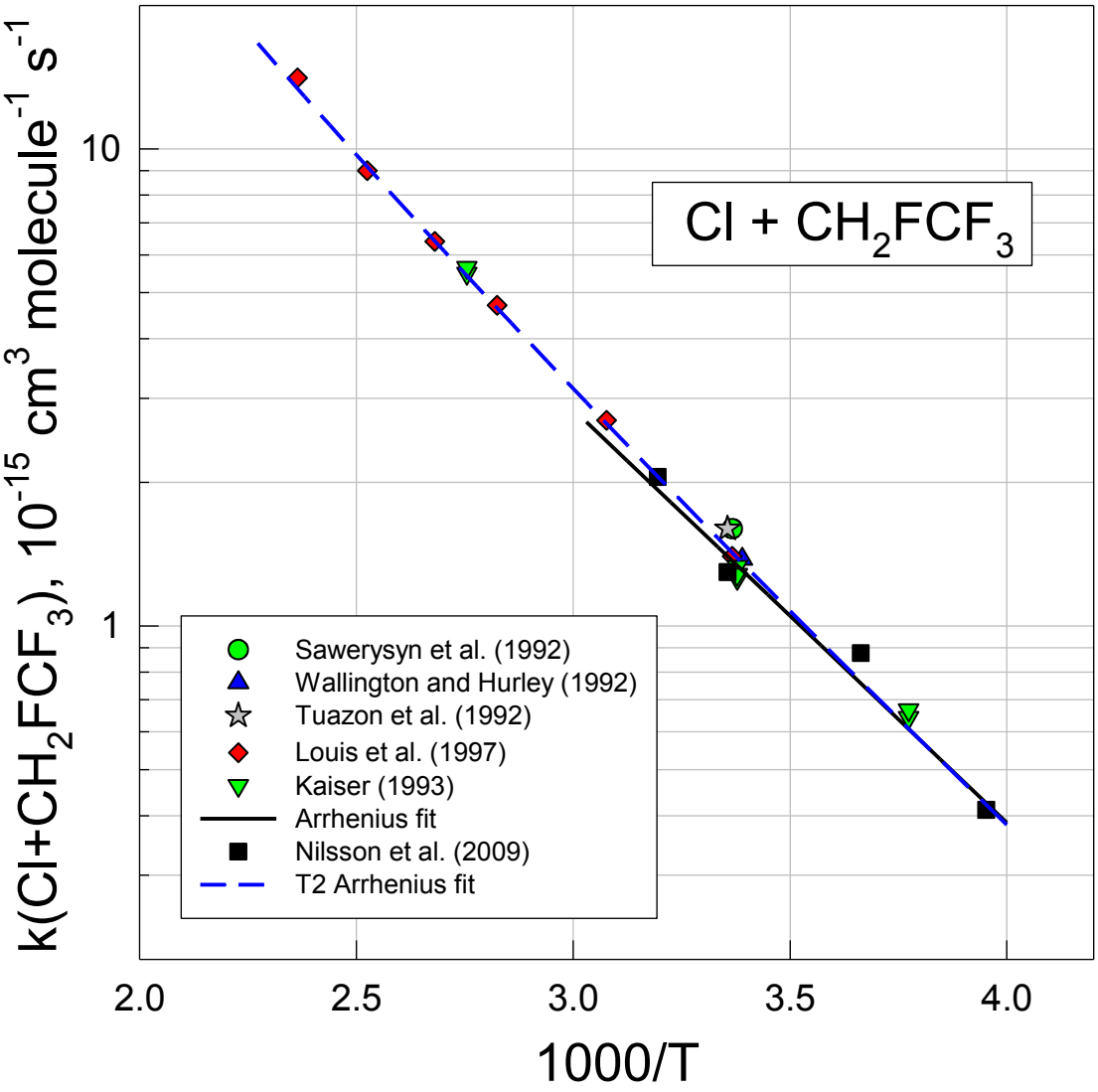
Louis, J., Talhaoui, A., Sawerysyn, J. P., Rayez, M.-T., and Rayez, J.-C.: J. Phys. Chem. A,. 101, 8503, 1997.

Nilsson, E. J. K., Johnson, M. S., Nielsen, O. J., Kaiser, E. W., Wallington T. J.: Int. J. Chem. Kinet., 41, 401, 2009.

Sawerysyn, J. P., Talhaoui, A., Meriaux, B., and Devolder, P.: Chem. Phys. Lett., 198, 197, 1992.

Tuazon, E. C., Atkinson, R., and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.

Wallington, T. J., and Hurley, M. D.: Chem. Phys. Lett., 189, 437, 1992.


Cl + CH2FCF3
k(Cl+CH2FCF3), 10-15 cm3 molecule-1 s-1
10
1
2.0
2.5
3.0
3.5
4.0
1000/T
Sawerysyn et al. (1992)
Wallington and Hurley (1992)
Tuazon et al. (1992)
Louis et al. (1997)
Kaiser (1993)
Arrhenius fit
Nilsson et al. (2009)
T2 Arrhenius fit