IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx25

 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 Kinetic Data Evaluation, http://iupac.pole-ether.fr.
This data sheet last evaluated: June 2015; last change in preferred values: December 2007.

$Cl + CH_3CHF_2$ (HFC-152a) $\rightarrow HCl + CH_3CF_2$ (1)
$\rightarrow HCl + CH_2CHF_2$ (2)

$\Delta H°(1) = -4.9$ kJ mol^{-1}
$\Delta H°(2) = 11.1$ kJ mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.54 \pm 0.25) \times 10^{-13}$	295	Taketani et al. (2005)	PLP-LIF (a)
Relative Rate Coefficients			
$k_1 = 7.0 \times 10^{-12} \exp(-965/T)$	280-360	Yano and Tschuikow-Roux, 1986	RR (b)
$k_1 = 2.7 \times 10^{-13}$	298		
$k_2 = 7.8 \times 10^{-12} \exp(-2399/T)$	280-360		
$k_2 = 2.5 \times 10^{-15}$	298		
$(2.4 \pm 0.7) \times 10^{-13}$	295	Wallington and Hurley, 1992	RR (c)
$(2.4 \pm 0.5) \times 10^{-13}$	298	Tuazon, et al., 1992	RR (d)
$k_1 = (2.35 \pm 0.31) \times 10^{-13}$	295	Taketani et al. (2005)	RR (e)
$k_2 = (1.92 \pm 0.30) \times 10^{-15}$	295		

Comments

(a) Laser photolysis of HCl at 193 nm as Cl atom source. Both Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$) detected by VUV-LIF.

(b) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were determined by GC and the measured rate coefficient ratios ratios of $k_1/k(Cl + C_2H_6) = 0.0835 \exp(866/T)$ and $k_2/k(Cl + C_2H_6) = 0.0932 \exp(2299/T)$ were placed on an absolute basis using $k(Cl + C_2H_6) = 8.3 \times 10^{-11} \exp(-100/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(c) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic measured by FTIR spectroscopy. The measured rate coefficient ratio is 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).

(d) Cl atoms were generated by the photolysis of Cl_2 in the presence of CH_3CHF_2 and CH_4 in 986 mbar of air. The decays of CH_3CHF_2 and CH_4 were measured by FTIR spectroscopy. The measured rate coefficient ratio $k(Cl + CH_3CHF_2)/k(Cl + CH_4) = 2.36 \pm 0.02$ is 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).

(e) Cl atoms were generated by the photolysis of Cl_2 in the UV irradiation of $CH_3CHF_2 - CH_4 - Cl_2$ and $CH_3CHF_2 - CH_3Cl - Cl_2$ in 920 mbar of N_2, or air, diluent. Ratios of $k(Cl + CH_3CHF_2)/k(Cl + CH_4) = 2.39 \pm 0.15$ and $k(Cl + CH_3CHF_2)/k(Cl + CH_3Cl) = 0.49 \pm 0.01$ were placed on an absolute basis using rate coefficients of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ and $k(Cl + CH_3Cl) = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) leading to a value of $k(Cl + CH_3CHF_2) = (2.37 \pm 0.31) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The UV irradiation of $CH_3CHF_2 - Cl_2 - N_2$ mixtures led to the formation of CH_3CF_2Cl and CH_2ClCHF_2 in molar yields of 99 ± 4 % and 0.81 ± 0.07 %, respectively. Rate coefficients in the table above were derived from the measured value of $k(Cl + CH_3CHF_2) = (2.37 \pm 0.31) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, the yield of $CH_2ClCHF_2 = k_2/k = 0.0081 \pm 0.0007$, and the assumption that $k_1/k + k_2/k = 1$.

Preferred Values

Parameter	Value	*T*/K
k_1 /cm^3 molecule^{-1} s^{-1}	2.5×10^{-13}	298
k_1 /cm^3 molecule^{-1} s^{-1}	$6.3 \times 10^{-12} \exp(-965/T)$	280-360
k_2 /cm^3 molecule^{-1} s^{-1}	2.3×10^{-15}	298
k_2 /cm^3 molecule^{-1} s^{-1}	$7.0 \times 10^{-12} \exp(-2400/T)$	280-360
Reliability		
$\Delta \log k_1$	± 0.15	298
$\Delta \log k_2$	± 0.15	298
$\Delta(E_1/R)$	± 500	
$\Delta(E_2/R)$	± 500	

Comments on Preferred Values

The recommended value of the overall rate constant at room temperature is an average of the absolute rate and all four relative rate studies, which show good agreement. The temperature dependence of k, k_1 and k_2 are taken from work of Yano and Tschuikow-Roux, (1986), which supersedes their previous data (Tschuikow-Roux et al. 1985).

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

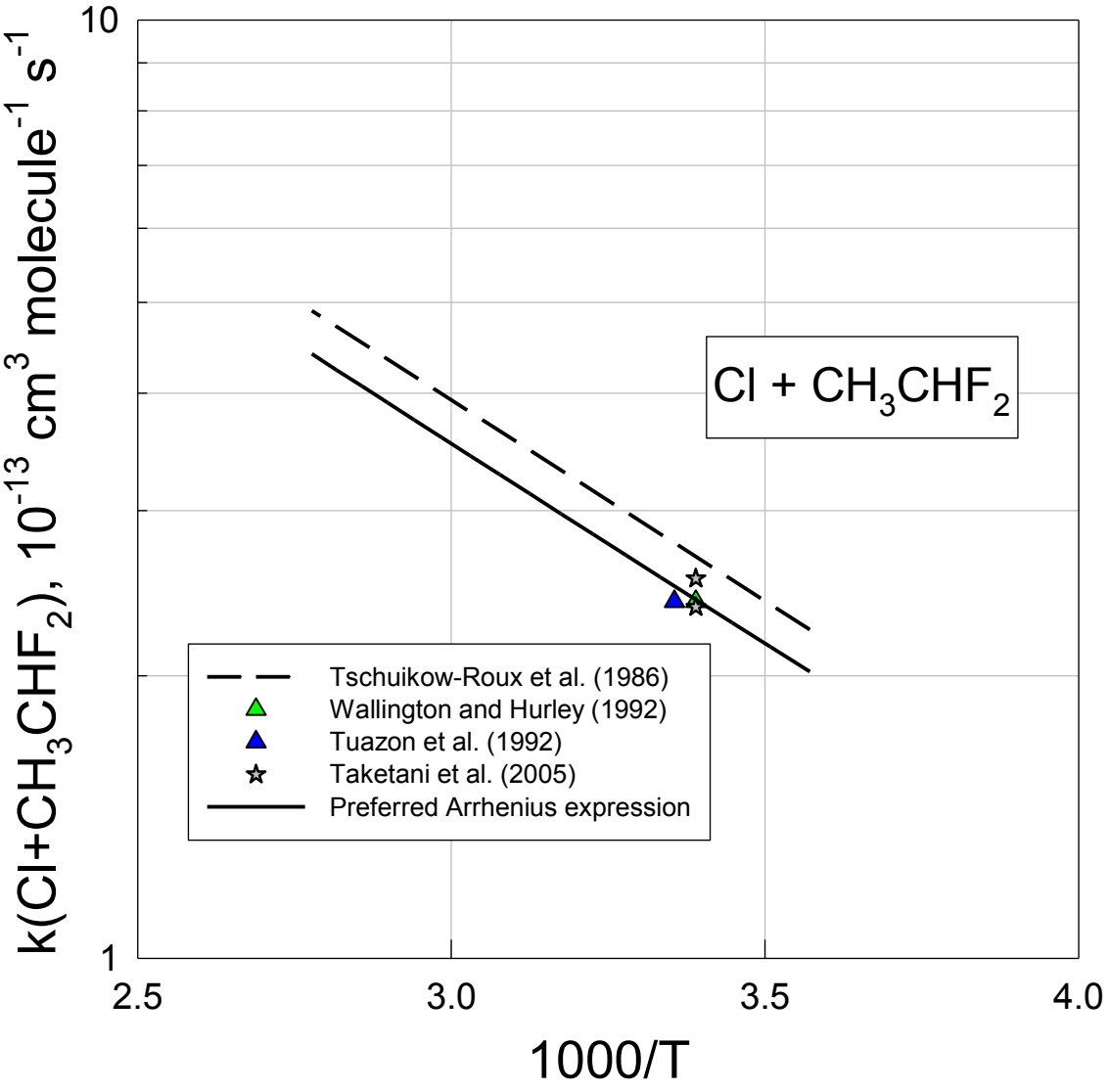
Taketani, F., Nakayama, T., Takahashi, K., Matsumi, Y., Hurley, M. D. Wallington, T. J., Toft, A., Sulbaek Andersen M. P.: J. Phys. Chem. A, 109, 9061, 2005.

Tschuikow-Roux, E., Yano, T. and Niedzielski, J.: J. Chem. Phys., 82, 65, 1985.

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.

Yano, T. and Tschuikow-Roux, E.: J. Photochem., 32, 25, 1986.


10
1
2.5
3.0
3.5
4.0
1000/T
k(Cl+CH3CHF2), 10-13 cm3 molecule-1 s-1
Cl + CH3CHF2
Tschuikow-Roux et al. (1986)
Wallington and Hurley (1992)
Tuazon et al. (1992)
Taketani et al. (2005)
Preferred Arrhenius expression