IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx38

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This datasheet last evaluated: June 2015; last change in preferred values: November 2003.

$HO + CH_2FCl$ (HCFC-31) $\rightarrow H_2O + CHFCl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.7 \pm 0.6) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$2.84 \times 10^{-12} \exp[-(1259 \pm 50)/T]$	245-375	Watson et al., 1977	FP-RF
$(4.21 \pm 0.41) \times 10^{-14}$	298		
$3.1 \times 10^{-12} \exp[-(1320 \pm 100)/T]$	273-373	Handwerk and Zellner, 1978	FP-RA
$(3.5 \pm 0.7) \times 10^{-14}$	293		
$(4.45 \pm 0.67) \times 10^{-14}$	297	Paraskevopoulos et al., 1981	FP-RA
$1.57 \times 10^{-19} T^{2.41} \exp[-(307 \pm 382)/T]$	250-486	Jeong and Kaufman, 1982;	DF-RF
$(4.94 \pm 0.30) \times 10^{-14}$	295	Jeong et al., 1984	
Relative Rate Coefficients			
$1.46 \times 10^{-12} \exp[-(1076 \pm 24)/T]$	293-371	DeMore, 1996	RR (a)
3.95×10^{-14}	298		

Comments

HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2O. CH_2Cl_2 was used as the reference compound. CH_2FCl and CH_2Cl_2 were monitored by FTIR spectroscopy, and a rate coefficient ratio of $k(HO + CH_2FCl)/k(HO + CH_2Cl_2) = 0.81 \exp[-(216 \pm 24)/T]$ was determined. This rate coefficient ratio is placed on an absolute basis using $k(HO + CH_2Cl_2) = 1.8 \times 10^{-12} \exp(-860/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.9×10^{-14}	298
k /cm^3 molecule^{-1} s^{-1}	$1.6 \times 10^{-12} \exp(-1105/T)$	240-300
Reliability		
$\Delta \log k$	± 0.1	298
$\Delta(E/R)$	± 200	240-300

Comments on Preferred Values

The absolute rate coefficients of Jeong and Kaufman (1982) are significantly higher than the absolute and relative rate data of Howard and Evenson (1976), Watson et al. (1977), Handwerk and Zellner, 1978), Paraskevopoulos et al. (1981) and DeMore (1996), with the discrepancies being more marked at the lowest temperatures studied by Jeong and Kaufman (250 and 295 K). The rate coefficients measured by Howard and Evenson (1976), Watson et al. (1977), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981) and DeMore (1996) are in reasonably good agreement, and the rate coefficients from these studies have been fitted to the three parameter expression $k = C\ T^2 \exp(-D/T)$, resulting in $k = 3.03 \times 10^{-18}\ T^2 \exp(-574/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 245-375 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C\ e^2\ T^2$ and $B = D + 2T$.

References

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

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Handwerk, V. and Zellner, R.: Ber. Bunsenges. Phys. Chem., 82, 1161, 1978.

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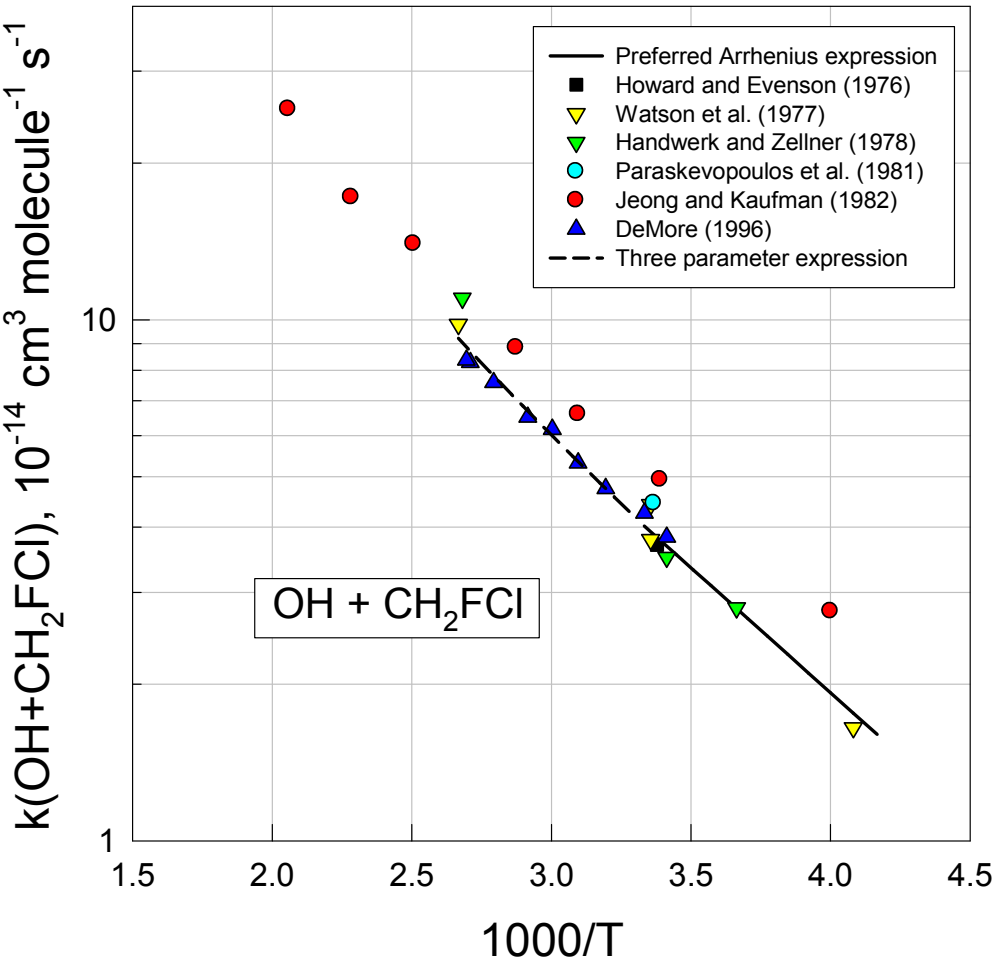
Watson, R. T., Machado, G., Conaway, B., Wagner, S. and Davis, D. D.: J. Phys. Chem., 81, 256, 1977.


Preferred Arrhenius expression
Howard and Evenson (1976)
Watson et al. (1977)
Handwerk and Zellner (1978)
Paraskevopoulos et al. (1981)
Jeong and Kaufman (1982)
DeMore (1996)
Three parameter expression
OH + CH2FCl
k(OH+CH2FCl), 10-14 cm3 molecule-1 s-1
1000/T
1
10
1.5
2.0
2.5
3.0
3.5
4.0
4.5