IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx51

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This data sheet last evaluated: June 2015; last change in preferred values: December 2007.

$HO + CH_2ClCF_3$ (HCFC-133a) $\rightarrow H_2O + CHClCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.05 \pm 0.23) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$1.1 \times 10^{-12} \exp[-(1260 \pm 60)/T]$	263-373	Handwerk and Zellner, 1978	FP-RA
$(1.5 \pm 0.3) \times 10^{-14}$	293		
$3.3 \times 10^{-11} \exp[-(2300 \pm 300)/T]$	294-427	Clyne and Holt, 1979	DF-RF
$(1.03 \pm 0.30) \times 10^{-14}$	294		
$3.06 \times 10^{-18} T^{1.91} \exp[-(644 \pm 313)/T]$	295-866	Fang et al., 1999	PLP-LIF
$(1.76 \pm 0.25) \times 10^{-14}$	295		
Relative Rate Coefficients			
$1.4 \times 10^{-13} \exp(-1503/T)$	298-360	DeMore, 2005	RR (a)
9.2×10^{-15}	298		

Comments

(a) OH radicals were generated by the 185 or 254 nm photolysis of O_3 in the presence of H_2O in argon diluent at atmospheric pressure. The loss of CH_2ClCF_3 was measured relative to CH_3CCl_3. At 298 K a rate coefficient ratio of $k(HO+CH_2ClCF_3)/k(HO+CH_3CCl_3) = 0.950$ was reported which can be combined with $k(HO+CH_3CCl_3) = 9.56 \times 10^{-15}$ (Atkinson et al., 2008) to give $k(HO+CH_2ClCF_3) = 9.08 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. The Arrhenius parameters in the table above were obtained from fitting the Arrhenius expression to the relative rate data from DeMore scaled to $k(HO+CH_3CCl_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.4×10^{-14}	298
k /cm^3 molecule^{-1} s^{-1}	$4.9 \times 10^{-13} \exp(-1065/T)$	260-380
Reliability		
$\Delta \log k$	± 0.25	298
$\Delta(E/R)$	± 200	260-380

Comments on Preferred Values

The temperature dependence of the rate coefficients obtained by Clyne and Holt (1979) is significantly higher than those measured by Handwerk and Zellner (1978) and Fang et al. (1999), and, as is the case for other haloalkanes, the data of Clyne and Holt (1979) are therefore not used in the evaluation. The rate coefficients of Fang et al. (1999) are consistently higher, by 10-20%, than those of Handwerk and Zellner over the temperature range common to both studies (295-373 K). The room temperature rate coefficients of Howard and Evenson (1976) and DeMore (2005) are in agreement, but are a factor of 1.5-2 below those of Handwerk and Zellner (1978) and Fang et al. (1999). The temperature dependence reported by DeMore (2005) is more pronounced than those observed by Handwerk and Zellner (1978) and Fang et al. (1999). The preferred Arrhenius expression is obtained from a unit-weighted least-squares analysis of the 260-380 K data of Howard and Evenson (1976), Handwerk and Zellner (1978), Fang et al. (1999), and DeMore (2005). Further studies are needed to reduce the considerable uncertainties in k(HO+CH_2ClCF_3) at, and below, 298 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., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 8, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr

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Fang, T. D., Taylor, P. H. and Berry, R. J.: J. Phys. Chem. A, 103, 2700, 1999.

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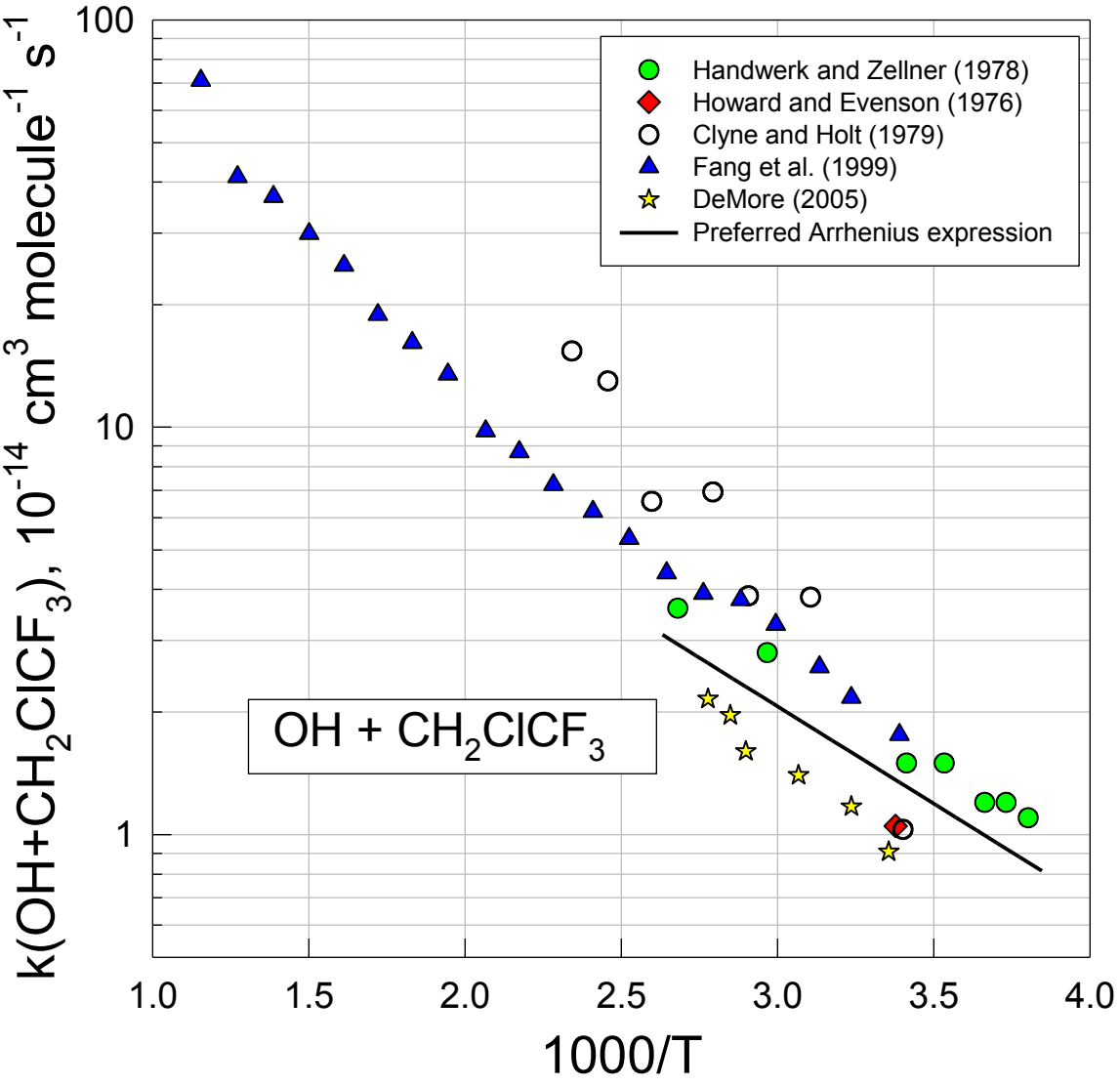
Handwerk and Zellner (1978)
Howard and Evenson (1976)
Clyne and Holt (1979)
Fang et al. (1999)
DeMore (2005)
Preferred Arrhenius expression
OH + CH2ClCF3
k(OH+CH2ClCF3), 10-14 cm3 molecule-1 s-1
1000/T
100
10
1
1.0
1.5
2.0
2.5
3.0
3.5
4.0