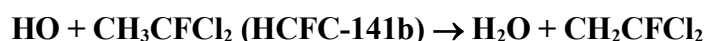


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx49

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



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$3.6 \times 10^{-13} \exp[-(1140 \pm 210)/T]$	243-400	Liu et al., 1990	FP-RF
$(7.01 \pm 1.2) \times 10^{-15}$	298		
$5.8 \times 10^{-13} \exp[-(1100 \pm 250)/T]$	238-426	Brown et al., 1990	DF-RF
$(1.61 \pm 0.55) \times 10^{-14}$	297		
$1.47 \times 10^{-12} \exp[-(1640 \pm 100)/T]$	253-393	Talukdar et al., 1991	PLP-LIF/ DF-LMR (a)
$(5.92 \pm 0.54) \times 10^{-15}$	298		
$(1.82 \pm 0.65) \times 10^{-15}$	250	Zhang et al., 1992	FP-RF (b)
$(2.01 \pm 0.90) \times 10^{-15}$	250		
$(3.39 \pm 0.82) \times 10^{-15}$	270		
$(4.80 \pm 1.46) \times 10^{-15}$	297		
$2.4 \times 10^{-12} \exp[-(1790 \pm 100)/T]$	298-479	Lancar et al., 1993	DF-EPR
$(5.7 \pm 1.5) \times 10^{-15}$	298		
$(4.6 \pm 0.8) \times 10^{-15}$	293	Mörs et al., 1996	FP-A
<i>Relative Rate Coefficients</i>			
$9.07 \times 10^{-21} T^{2.82} \exp[-(798 \pm 105)/T]$	298-358	Huder and DeMore, 1993	RR (c,d)
5.91×10^{-15}	298		
$1.78 \times 10^{-18} T^2 \exp[-(984 \pm 28)/T]$	298-358	Huder and DeMore, 1993	RR (c,e)
5.85×10^{-15}	298		

Comments

- (a) Experiments were carried out down to 233 K, using highly purified samples. In the pulsed laser photolysis experiments, photolysis of HONO was used as the HO radical source to avoid photolysis of CH₃CFCl₂. An Arrhenius plot of the entire data set showed curvature at the two lowest temperatures studied (233 and 249 K), and the cited Arrhenius expression was derived using only the rate coefficients measured at ≥ 253 K.
- (b) HO radicals were generated by the pulsed photolysis of H₂O. Experiments carried out with reduced flash energies or water vapor concentrations (resulting in lower initial HO radical concentrations) led to the lower measured rate coefficients cited in the table. These data supersede those of Liu et al. (1990) at 243-298 K.
- (c) HO radicals were generated by the photolysis of H₂O-O₃ mixtures at 254 nm in H₂O-O₃-CH₃CFCl₂-CH₄ (or CH₃CCl₃)-Ar-O₂ mixtures. The concentrations of CH₃CFCl₂ and CH₄ (or CH₃CCl₃) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{CFCl}_2)/k(\text{HO} + \text{CH}_4) = (0.49 \pm 0.16) \exp[(189 \pm 105)/T]$ and $k(\text{HO} + \text{CH}_3\text{CFCl}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = (0.79 \pm 0.07) \exp[-(74 \pm 28)/T]$ are placed on an absolute basis using $k(\text{HO} + \text{CH}_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008) and $k(\text{HO} + \text{CH}_3\text{CCl}_3)$

$$= 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (Atkinson et al., 2008).}$$

(d) Relative to $k(\text{HO} + \text{CH}_4)$.

(e) Relative to $k(\text{HO} + \text{CH}_3\text{CCl}_3)$.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.8×10^{-15}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$8.1 \times 10^{-13} \exp(-1470/T)$	220-300
<i>Reliability</i>		
$\Delta \log k$	± 0.10	298
$\Delta(E/R)$	± 200	220-300

Comments on Preferred Values

The absolute rate coefficients of Brown et al. (1990) are higher than those from the absolute rate studies of Liu et al. (1990), Talukdar et al. (1991), Zhang et al. (1992), Lancar et al. (1993) and Mörs et al. (1996) at all temperatures studied, and the rate coefficients of Liu *et al.* (1990) at temperatures ≤ 298 K are significantly higher than those of Talukdar et al. (1991), Zhang et al. (1992), Lancar et al. (1993) and Mörs et al. (1996). The measurements of Zhang et al. (1992) show that the earlier lower temperature (≤ 298 K) data of Liu et al. (1990) were in error due to the occurrence of secondary reactions of HO radicals with reaction products. The rate coefficients of Talukdar et al. (1991), Zhang et al. (1992) [obtained at low flash energies and/or low water vapor concentrations and with high associated uncertainties], Lancar et al. (1993), Mörs et al. (1996) and Huder and DeMore (1993) are in good agreement, as are those of Talukdar et al. (1991) and Liu et al. (1990) at temperatures ≥ 330 K.

The rate coefficients of Talukdar et al. (1991), Zhang et al. (1992), Lancar et al. (1993) and Mörs et al. (1996) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.68 \times 10^{-18} T^2 \exp(-962/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 233-479 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 255 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The rate coefficients of Huder and DeMore (1993) over the temperature range 298-358 K, obtained relative to the reactions of HO radicals with CH_4 and CH_3CCl_3 , agree to within 6% with those calculated from the preferred three parameter expression.

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