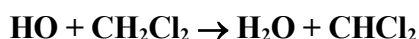


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx39

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. 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: November 2003.



$$\Delta H^\circ = -94.6 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.55 \pm 0.34) \times 10^{-13}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$(1.45 \pm 0.20) \times 10^{-13}$	298.5	Perry et al., 1976	FP-RF
$4.27 \times 10^{-12} \exp[-(1094 \pm 82)/T]$	245-375	Davis et al., 1976	FP-RF
$(1.16 \pm 0.05) \times 10^{-13}$	298		
$1.61 \times 10^{-19} T^{2.54} \exp[-(186 \pm 493)/T]$	251-455	Jeong and Kaufman, 1982;	DF-RF
$(1.53 \pm 0.095) \times 10^{-13}$	292	Jeong et al., 1984	
$4.01 \times 10^{-15} T^{1.09} \exp[-(771 \pm 48)/T]$	295-955	Taylor et al., 1993	PLP-LIF (a)
$(1.47 \pm 0.18) \times 10^{-13}$	295		
$2.61 \times 10^{-12} \exp[-(944 \pm 29)/T]$	277-370	Villenave et al., 1997	FP-RF
$(1.10 \pm 0.05) \times 10^{-13}$	298		
$6.6 \times 10^{-13} T^{0.5} \exp[-(721 \pm 32)/T]$	219-394	Herndon et al., 2001	PLP-LIF
$(1.00 \pm 0.14) \times 10^{-13}$	298		
<i>Relative Rate Coefficients</i>			
9.5×10^{-14}	298	Cox et al., 1976	RR (b)
$2.72 \times 10^{-18} T^2 \exp[-(286 \pm 29)/T]$	293-360	Hsu and DeMore, 1994	RR (c,d)
9.25×10^{-14}	298		
$1.96 \times 10^{-18} T^2 \exp[-(104 \pm 20)/T]$	298-368	Hsu and DeMore, 1994	RR (c,e)
1.22×10^{-13}	298		

Comments

- (a) These data supersede the earlier data from this group (Taylor et al., 1989).
- (b) HO radicals were generated by the photolysis of HONO-air mixtures at 1.013 bar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the effect of CH₂Cl₂ on NO formation and a rate coefficient for the reaction of HO radicals with CH₄ of $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson et al., 2006), the rate coefficient cited in the table is obtained.
- (c) HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor. CH₂Cl₂ and CH₃CHF₂ (or CH₃CH₂F) concentrations were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CH}_2\text{Cl}_2)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.97 \pm 0.09) \exp[(294 \pm 29)/T]$ and $k(\text{HO} + \text{CH}_2\text{Cl}_2)/k(\text{HO} + \text{CH}_3\text{CH}_2\text{F}) = (0.32 \pm 0.02) \exp[(171 \pm 20)/T]$ are placed on an absolute basis by using rate coefficients of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

(Atkinson et al., 2008) and $k(\text{HO} + \text{CH}_3\text{CH}_2\text{F}) = 6.12 \times 10^{-18} T^2 \exp(-275/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008).

(d) Relative to $\text{HO} + \text{CH}_3\text{CHF}_2$.

(e) Relative to $\text{HO} + \text{CH}_3\text{CH}_2\text{F}$.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.0×10^{-13}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.8 \times 10^{-12} \exp(-860/T)$	210-400
<i>Reliability</i>		
$\Delta \log k$	± 0.1	298
$\Delta(E/R)$	± 150	210-400

Comments on Preferred Values

The absolute room temperature rate coefficients of Howard and Evenson (1976), Perry et al. (1976), Jeong and Kaufman (1982) and Taylor et al. (1993) are significantly higher than those of Davis et al. (1976), Villenave et al. (1997) and Herndon et al. (2001), possibly because of the presence of reactive impurities (including stabilizers) present in the CH_2Cl_2 samples used (Villenave et al., 1997; Herndon et al., 2001). The relative rate data of Cox et al. (1976) and Hsu and DeMore (1994) are in reasonable agreement with the absolute rate coefficients of Villenave et al. (1997) and Herndon et al. (2001). An Arrhenius plot of the absolute rate data of Villenave et al. (1997) and Herndon et al. (2001) shows little or no evidence for curvature over the temperature range studied (219-394 K). Accordingly, the preferred Arrhenius expression is obtained from a unit-weighted least-squares analysis of the absolute rate coefficients of Villenave et al. (1997) and Herndon et al. (2001). The room temperature relative rate constant of Cox et al. (1976) agrees well with the preferred 298 K value, while the rate coefficients of Hsu and DeMore (1994) relative to $\text{HO} + \text{CH}_3\text{CHF}_2$ are ~5-10% lower than the preferred values and those relative to $\text{HO} + \text{CH}_3\text{CH}_2\text{F}$ are ~15-20% higher than the preferred values over the temperature ranges 298-360 K and 298-368 K, respectively.

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