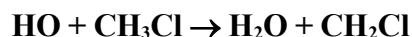


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oClOx37; IV.A2.111

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.



$$\Delta H^\circ = -79.8 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.6 \pm 0.8) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$4.1 \times 10^{-12} \exp[-(1359 \pm 151)/T]$	298-423	Perry et al., 1976	FP-RF
$(4.4 \pm 0.5) \times 10^{-14}$	298		
$1.84 \times 10^{-12} \exp[-(1098 \pm 36)/T]$	250-350	Davis et al., 1976	FP-RF
$(4.29 \pm 0.21) \times 10^{-14}$	298		
$(4.10 \pm 0.69) \times 10^{-14}$	297	Paraskevopoulos et al., 1981	FP-RA
$2.21 \times 10^{-21} T^{3.08} \exp[-(232 \pm 423)/T]$	247-483	Jeong and Kaufman, 1982;	DF-RF
$(3.95 \pm 0.26) \times 10^{-14}$	293	Jeong et al., 1984	
$(5.3 \pm 0.8) \times 10^{-14}$	298	Brown et al., 1990	DF-RF
$2.90 \times 10^{-14} T^{0.89} \exp[-(1447 \pm 75)/T]$	295-955	Taylor <i>et al.</i> , 1993	PLP-LIF (a)
$(4.9 \pm 0.6) \times 10^{-14}$	295		
$1.24 \times 10^{-13} T^{0.5} \exp[-(1210 \pm 52)/T]$	224-398	Herndon et al., 2001	PLP-LIF
$(3.32 \pm 0.10) \times 10^{-14}$	298		
$3.90 \times 10^{-12} \exp[-(1411 \pm 85)/T]$	298-460	Orkin et al., 2013	DF-EPR (b)
$(3.36 \pm 0.17) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
7.8×10^{-14}	298	Cox et al., 1976	RR (c)
$5.35 \times 10^{-18} T^2 \exp[-(775 \pm 74)/T]$	293-358	Hsu and DeMore, 1994	RR (d)
3.53×10^{-14}	298		

Comments

- These data supersede the earlier data from this group (Taylor et al., 1989).
- HO radicals were generated by the reaction of H atoms with NO₂ in 0.4 kPa (3.0 Torr) of He diluent in a discharge flow system. Decay of HO radical concentration was monitored by EPR.
- HO radicals were generated by the photolysis of HONO-air mixtures at one atmosphere total 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 CH₃Cl 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.
- HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor. The

concentrations of CH₃Cl and CH₃CHF₂ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{Cl})/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (1.91 \pm 0.45) \exp[-(195 \pm 74)/T]$ is placed on an absolute base by using a rate coefficient 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).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	3.6×10^{-14}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.1 \times 10^{-12} \exp(-1210/T)$	220-300
<i>Reliability</i>		
$\Delta \log k$	0.08	298
$\Delta(E/R)$	± 200	220-300

Comments on Preferred Values

At room temperature, the absolute rate coefficients of Perry et al. (1976), Davis et al. (1976), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982), Brown et al. (1990), Taylor et al. (1993), Herndon et al. (2001), and Orkin et al. (2013) and the relative rate coefficients of Cox et al. (1976) and Hsu and DeMore (1994) are in agreement within the likely combined experimental uncertainties. Furthermore, the relative rate coefficients of Hsu and DeMore (1994) are in excellent agreement with the absolute rate coefficients of Herndon et al. (2001) and Orkin et al. (2013) over the temperature range common to both studies (293-358 K). At 363 and 401 K the rate coefficients of Jeong and Kaufman (1982) are in good agreement with the data of Herndon et al. (2001) and Orkin et al. (2013). The three parameter equation $k = CT^2 \exp(-D/T)$ was fit to the absolute rate coefficients of Herndon et al. (2001) resulting in $k = 4.34 \times 10^{-18} T^2 \exp(-700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 224-398 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 $B = D + 2T$. As noted above, the rate coefficients obtained from the relative rate study of Hsu and DeMore (1994) are in excellent agreement with the preferred values.

Gola et al. (2005) have measured a rate constant ratio of $k(\text{HO} + {}^{12}\text{CH}_3\text{Cl})/k(\text{HO} + {}^{13}\text{CH}_3\text{Cl}) = 1.059 \pm 0.008$ at $298 \pm 2 \text{ K}$, and the deuterium isotope effect for the reaction of HO radicals with CD₃Cl, of $k(\text{HO} + \text{CH}_3\text{Cl})/k(\text{HO} + \text{CD}_3\text{Cl}) = 3.9 \pm 0.4$ at $298 \pm 2 \text{ K}$.

References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>
- 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>
- Brown, A. C., Canosa-Mas, C. E. and Wayne, R. P.: Atmos. Environ., 24A, 361, 1990.
- Cox, R. A., Derwent, R. G., Eggleton, A. E. J. and Lovelock, J. E.: Atmos. Environ., 10, 305, 1976.
- Davis, D. D., Machado, G., Conaway, B., Oh, Y. and Watson, R. T.: J. Chem. Phys., 65, 1268, 1976.
- Gola, A. A., D'Anna, B., Feilberg, K. L., Sellevåg, S. R., Bache-Andreassen, L. and Nielsen, C. J.: Atmos. Chem. Phys. 5, 2395, 2005.
- Herndon, S. C., Gierczak, T., Talukdar, R. K. and Ravishankara, A. R.: Phys. Chem. Chem.

Phys., 3, 4529, 2001.

Howard, C. J. and Evenson, K. M.: J. Chem. Phys., 64, 197, 1976.

Hsu, K.-J. and DeMore, W. B.: Geophys. Res. Lett., 21, 805, 1994.

Jeong, K.-M. and Kaufman, F.: J. Phys. Chem., 86, 1808, 1982.

Jeong, K.-M., Hsu, K.-J., Jeffries, J. B. and Kaufman, F.: J. Phys. Chem., 88, 1222, 1984.

Orkin, V.L., Khamaganov, V.G., Kasimovskaya, E.E. and Guschin, A.G.: J. Phys. Chem. A, 117, 5483, 2013.

Perry, R. A., Atkinson, R. and Pitts, J. N., Jr.: J. Chem. Phys., 64, 1618, 1976.

Taylor, P. H., Jiang, Z. and Dellinger, B.: Int. J. Chem. Kinet., 25, 9, 1993.

Taylor, P. H., D'Angelo, J. A., Martin, M. C., Kasner, J. H. and Dellinger, B.: Int. J. Chem. Kinet., 21, 829, 1989.

