

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC27

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.

This data sheet last evaluated: 2nd August 2007; no revision of preferred values.

HO + CH₃CH₂CH₂CH₂OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(8.31 \pm 0.63) \times 10^{-12}$	296	Wallington and Kurylo, 1987	FP-RF
$(7.80 \pm 0.20) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
$5.30 \times 10^{-12} \exp[(146 \pm 92)/T]$	263-372	Yujing and Mellouki, 2001	PLP-LIF
$(8.47 \pm 0.34) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(6.8 \pm 1.3) \times 10^{-12}$	292	Campbell et al., 1976	RR (a)
$(7.97 \pm 0.66) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (b)
$(1.03 \pm 0.05) \times 10^{-11}$	298 ± 2	Oh and Andino, 2001	RR (c)
$(7.67 \pm 0.14) \times 10^{-12}$	298 ± 2	Cavalli et al., 2002	RR (b)
$(8.58 \pm 0.66) \times 10^{-12}$	295 ± 2	Wu et al., 2003	RR (d)

Comments

- HO radicals were generated by the dark reaction of H₂O₂-NO₂ mixtures in the presence of CO and an organic compound. From sequential experiments using *n*-butane and 1-butanol, a rate coefficient ratio of $k(\text{HO} + 1\text{-butanol})/k(\text{HO} + n\text{-butane}) = 3.00 \pm 0.56$ (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + n\text{-butane}) = 2.28 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 292 K (IUPAC, current recommendation).
- HO radicals were generated by the photolysis of CH₃ONO in air, and the concentrations of 1-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + 1\text{-butanol})/k(\text{HO} + \text{cyclohexane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003) [Cavalli et al. (2002) measured a rate coefficient ratio of $k(\text{HO} + 1\text{-butanol})/k(\text{HO} + \text{cyclohexane}) = 1.10 \pm 0.02$].
- HO radicals were generated by the photolysis of CH₃ONO in air, and the concentrations of 1-butanol and *p*-xylene (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + 1\text{-butanol})/k(\text{HO} + p\text{-xylene}) = 0.72 \pm 0.03$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + p\text{-xylene}) = 1.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Calvert et al., 2002).
- HO radicals were generated by the photolysis of H₂O₂ in 1 atmosphere of air at 254 nm. The concentrations of 1-butanol and propane (the reference compound) were measured by GC. The measured rate coefficient ratio, $k(\text{HO} + 1\text{-butanol})/k(\text{HO} + \text{propane})$, is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{propane}) = 1.07 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson, 2003; IUPAC, current recommendation).

Preferred Values

$k = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 5.3 \times 10^{-12} \exp(140/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260-380 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K

Comments on Preferred Values

The absolute rate study of Yujing and Mellouki (2001), the sole temperature-dependence study, is used to derive the preferred values. The 298 K coefficient from the study of Yujing and Mellouki (2001) is in good agreement with the room temperature absolute and relative rate coefficients of Wallington and Kurylo (1987), Nelson et al. (1990), Cavalli et al. (2002) and Wu et al. (2003), but is 18% lower than the relative rate coefficient of Oh and Andino (2001). The experimental technique of Campbell et al. (1976) was possibly prone to unrecognized problems.

References

- Atkinson, R.: *Atmos. Chem. Phys.* 3, 2233, 2003.
- Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J. and Yarwood, G.: *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*, Oxford University Press, New York, NY, 2002.
- Campbell, I. M., McLaughlin, D. F. and Handy, B. J.: *Chem. Phys. Lett.* 38, 362, 1976.
- Cavalli, F., Geiger, H., Barnes, I. and Becker, K. H.: *Environ. Sci. Technol.* 36, 1263, 2002.
- IUPAC: <http://iupac.pole-ether.fr>, 2013.
- Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J. and Nielsen, O. J.: *Int. J. Chem. Kinet.* 22, 1111, 1990.
- Oh, S. and Andino, J. M.: *Int. J. Chem. Kinet.* 33, 422, 2001.
- Wallington, T. J. and Kurylo, M. J.: *Int. J. Chem. Kinet.* 19, 1015, 1987.
- Wu, H., Mu, Y., Zhang, X. and Jiang, G.: *Int. J. Chem. Kinet.* 35, 81, 2003.
- Yujing, M. and Mellouki, A.: *Chem. Phys. Lett.* 333, 63, 2001.