

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC25

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

HO + CH₃CH₂CH₂OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(5.33 \pm 0.54) \times 10^{-12}$	296 ± 2	Overend and Paraskevopoulos, 1978	FP-RA
$(5.34 \pm 0.39) \times 10^{-12}$	296	Wallington and Kurylo, 1987	FP-RF
$(5.64 \pm 0.48) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
$4.68 \times 10^{-12} \exp[(68 \pm 41)/T]$	263-372	Yujing and Mellouki, 2001	PLP-LIF
$(5.83 \pm 0.18) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(3.8 \pm 0.7) \times 10^{-12}$	292	Campbell et al., 1976	RR (a)
$(5.12 \pm 0.41) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (b)
$(4.42 \pm 0.26) \times 10^{-12}$	298 ± 2	Oh and Andino, 2000	RR (c,d)
$(6.44 \pm 0.43) \times 10^{-12}$	298 ± 2	Oh and Andino, 2000	RR (c,e)
$(5.11 \pm 0.19) \times 10^{-12}$	273	Cheema et al., 2002	RR (f)
$(5.50 \pm 0.17) \times 10^{-12}$	298		
$(5.74 \pm 0.33) \times 10^{-12}$	313		
$(6.20 \pm 0.17) \times 10^{-12}$	343		
$(5.42 \pm 0.44) \times 10^{-12}$	295 ± 2	Wu et al., 2003	RR (g)

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-propanol, a rate coefficient ratio of $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + n\text{-butane}) = 1.67 \pm 0.27$ (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-propanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + \text{cyclohexane})$ 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).
- HO radicals were generated by the photolysis of CH₃ONO in air, and the concentrations of 1-propanol and *n*-hexane and *p*-xylene (the reference compounds) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + n\text{-hexane}) = 0.85 \pm 0.05$ and $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + p\text{-xylene}) = 0.45 \pm 0.03$ are placed on an absolute basis by use of rate coefficients of $k(\text{HO} + n\text{-hexane}) = 5.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + p\text{-xylene}) = 1.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003; Calvert et al., 2002).
- Relative to HO + *n*-hexane.
- Relative to HO + *p*-xylene.

- (f) HO radicals were generated by the photolysis of CH₃ONO in air, and the concentrations of 1-propanol and 2,3-dimethylbutane (the reference compound) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + 2,3\text{-dimethylbutane})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2,3\text{-dimethylbutane}) = 1.66 \times 10^{-17} T^2 \exp(407/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).
- (g) HO radicals were generated by the photolysis of H₂O₂ in 1 atmosphere of air at 254 nm. The concentrations of 1-propanol and propane (the reference compound) were measured by GC. The measured rate coefficient ratio, $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + \text{propane})$, 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

$k = 5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 4.6 \times 10^{-12} \exp(70/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260-380 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred values are based on the temperature-dependent absolute rate study of Yujing and Mellouki (2001). At room temperature, the rate coefficients measured by Yujing and Mellouki (2001) are in good agreement with the absolute rate coefficients of Overend and Paraskevopoulos (1976), Wallington and Kurylo (1987) and Nelson et al. (1990), and with the relative rate constants of Nelson et al. (1990) and Wu et al. (2003). The experimental technique of Campbell et al. (1976) was possibly prone to unrecognized problems, and the relative rate constants of Oh and Andino (2000) measured relative to *n*-hexane and *p*-xylene are respectively 25% higher and 11% lower than the preferred value. The rate coefficients determined by Cheema et al. (2002) relative to that for 2,3-dimethylbutane are in good agreement with the preferred values (to within 15%), although the Cheema et al. (2002) data indicate a positive temperature dependence in contrast to that observed by Yujing and Mellouki (2001) and used as the basis for the preferred values.

References

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