IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC79

This data sheet last evaluated: June 2016; last change in preferred values: June 2016.

$HO + CH_3C(O)CH(OH)CH_3 \rightarrow H_2O + CH_3C(O)C(OH)CH_3$ (1)

$HO + CH_3C(O)CH(OH)CH_3 \rightarrow$ products (2)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(9.3 \pm 2.0) \times 10^{-12}$	296 ± 2	Aschmann et al., 2000	RR-GC (a)
$(2.25 \pm 0.20) \times 10^{-12} \exp[(612 \pm 50)/T]$	298-338	Messaadia et al., 2013	RR-FTIR (b)
$(10.1 \pm 3.2) \times 10^{-12}$	298		

Comments

(a) HO radicals were generated by the irradiation of CH_3ONO-NO-air mixtures at 986 mbar (740 Torr) total pressure of purified air at ~5% humidity at $\lambda > 300$ nm. Experiments were carried out in a 7900 liter Teflon chamber. The concentrations of 3-hydroxy-2-butanone and n-octane (the reference compound) were measured by gas chromatography. The measured rate coefficient ratio of k(HO + 3-hydroxy-2-butanone)/k(HO + n-octane) = 1.19 ± 0.05 is placed on an absolute basis using k(HO + n-octane) = 7.81×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K and atmospheric pressure (Calvert et al., 2008).

(b) HO radicals were generated by the irradiation of HONO-air mixtures at 800-1013 mbar (600-760 Torr) of air at $400 > \lambda > 300$ nm. Experiments were carried out in a 63 liter triple-jacket Pyrex chamber. The concentrations of 3-hydroxy-2-butanone and benzaldehyde (the reference compound) were measured by FTIR. The measured rate coefficient ratio of k(HO + 3-hydroxy-2-butanone)/k(HO + benzaldehyde) = 0.80 ± 0.05 (at 298K), 0.70 ± 0.03 (at 313K), 0.72 ± 0.06 (at 338K) are placed on an absolute basis using k(HO + benzaldehyde) = $6.8 \times 10^{-12} \exp(185/T)$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2011).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	9.7×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	1.24×10^{-12} exp (612/T)	280-350
Reliability		
$\Delta \log k$	± 0.1	298
Δ E/R	± 350	

Comments on Preferred Values

The results reported by Aschmann et al. (2000) and Messaadia et al. (2013) are in good agreement. Taking an average of the results from the two studies gives the recommended value of $k = 9.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. Fitting the Arrhenius expression to the data from Messaadia et al. (2013) and adjusting the A-factor to reproduce the recommended value at 298 K gives k(OH+$CH_3C(O)CH(OH)CH_3$) = 1.24×10^{-12} exp(612/T) cm^3 molecule^{-1} s^{-1}. In the product study by Aschmann et al. (2000) of the HO initiated oxidation of 3-hydroxy-2-butanone it was observed that 2,3-butanedione (biacetyl) was formed in a molar yield of 0.79 ± 0.14. The reaction proceeds mainly via hydrogen atom abstraction from the tertiary C-H bond:

$$HO + CH_3C(O)CH(OH)CH_3 \rightarrow CH_3C(O)C(OH)CH_3 + H_2O$$
$$CH_3C(O)C(OH)CH_3 + O_2 \rightarrow CH_3C(O)C(O)CH_3 + HO_2$$

The other possible channel is the H-atom abstraction from the methyl group which may account for about 20 %.

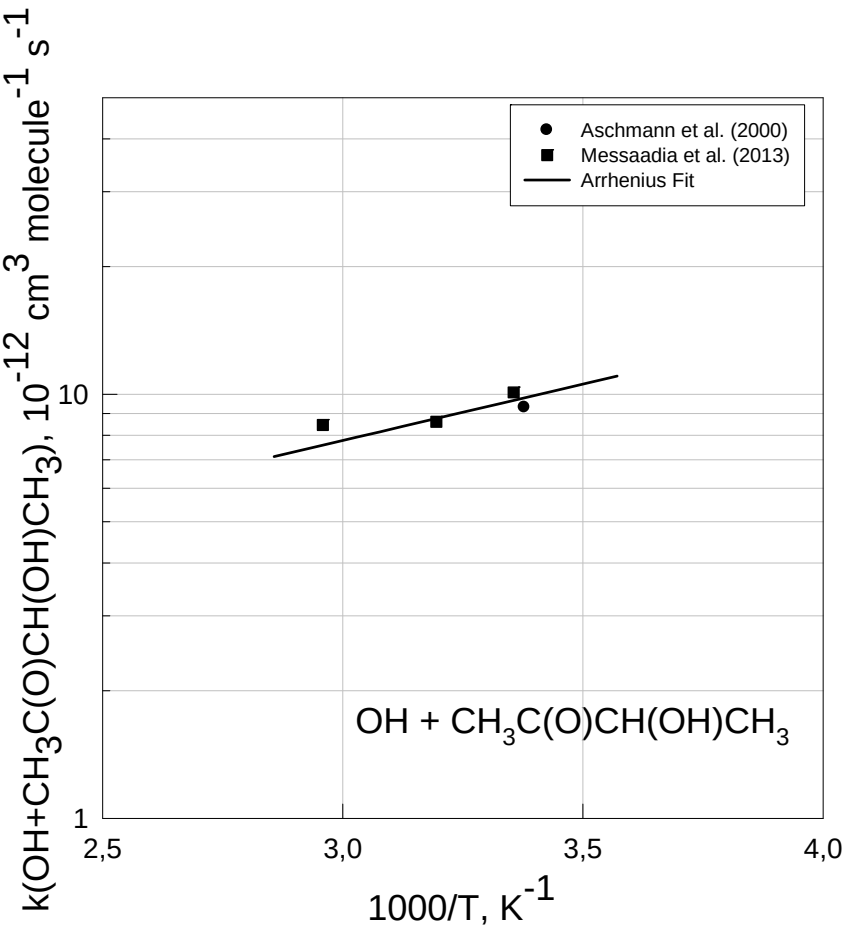
References

Aschmann, S. M., Arey, J., and Atkinson, R.: J. Phys. Chem. A, 104, 3998, 2000.

Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S., and Wallington, T. J.: *The Mechanisms of Atmospheric Oxidation of the Alkanes*, Oxford University Press, New York, 2008.

Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and Wallington, T. J.: *The Mechanisms of Atmospheric Oxidation of the Oxygenates*, Oxford University Press, New York, 2011.

Messaadia, L., El Dib, G., Cazaunau, M., Roth, E., Ferhati, A., Mellouki, A., and Chakir, A.: Atmos. Env., 77, 951, 2013.


Aschmann et al. (2000)
Messaadia et al. (2013)
Arrhenius Fit
OH + CH3C(O)CH(OH)CH3
k(OH+CH3C(O)CH(OH)CH3), 10-12 cm3 molecule-1 s-1
1000/T, K-1
10
1
2,5
3,0
3,5
4,0