IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC68

This data sheet last evaluated: June 2009.

HO + *i*-$C_3H_7CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.8\pm0.3) \times 10^{-12} \exp[(393 \pm 125)/T]$	255-423	Semmes et al., 1985	FP-RF (a)
$(2.42 \pm 0.33) \times 10^{-11}$	298		
$(15.8\pm0.5.0) \times 10^{-12} \exp[(313 \pm 145)/T]$	298-519	Dóbé et al., 1989	DF-RF (b)
$(4.63 \pm 0.73) \times 10^{-11}$	298		
$(7.3\pm1.9) \times 10^{-11} \exp[(390 \pm 78)/T]$	243-372	Thévenet et al., 2000	PLP-LIF (c)
$(2.6 \pm 0.4) \times 10^{-11}$	298		
Relative Rate Coefficients			
$(1.68 \pm 0.20) \times 10^{-11}$	298	Audley et al., 1981	RR (d, h)
$(2.69 \pm 0.52) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981	RR (e, i)
$(2.78 \pm 0.26) \times 10^{-11}$	297 ± 3	Stemmler et al., 1997	RR (f, j)
$(2.64 \pm 0.22) \times 10^{-11}$	298 ± 2	D'Anna et al., 2001	RR (g, k)

Comments

(a) HO radicals were generated by the vacuum ultraviolet (λ ≥ 165 nm) photolysis of H_2O and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(b) HO radicals were generated by the reaction H + NO_2 and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(c) HO radicals were generated by the photolysis of H_2O_2 and their concentration was measured by pulsed laser induced fluorescence.

(d) HO radicals were generated by the dark reaction of H_2O_2-NO_2 mixtures in the presence of CO and an organic compound. From sequential experiments using acetaldehyde and *iso*-butyraldehyde, a rate coefficient ratio of k(HO + *iso*-butyraldehyde)/k(HO + acetaldehyde) = 1.12 ± 0.13 (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis using k(HO + acetaldehyde) = 1.5×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson et al., 2006).

(e) HO radicals were generated by the photolysis of HONO at λ = 300-450 nm in air at atmospheric pressure in a 220 L Tedlar chamber. The concentrations of *iso*-butyraldehyde and ethene (the reference compound) were measured by GC-FID. The measured rate coefficient ratio of k(HO + *iso*-butyraldehyde)/k(HO + ethene) = 3.40 ± 0.66 is placed on an absolute basis using k(HO + ethene) = 7.9×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson et al., 2006).

(f) HO radicals were generated by the photolysis of CH_3ONO at λ = 350-450 nm in air at 725 ± 25 Torr (967 ± 33 mbar) pressure in a 200 L Teflon chamber. The concentrations of *iso*-butyraldehyde and di-n-propyl ether (the reference compound) were measured by GC. The measured rate coefficient ratio of *k*(HO + *iso*-butyraldehyde)/*k*(HO + di-n-propyl ether) = 1.39 ± 0.04 is placed on an absolute basis by use of a rate coefficient of *k*(HO + di-n-propyl ether) = 2.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K and atmospheric pressure (Calvert et al., 2010).

(g) HO radicals were generated by the photolysis of an organic nitrite in air at 1013 ± 10 mbar pressure in a 250 L electropolished stainless-steel reactor. The concentrations of *iso*-butyraldehyde and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of *k*(HO + *iso*-butyraldehyde)/*k*(HO + 1-butene) = 0.85 ± 0.07 is placed on an absolute basis by use of a rate coefficient of *k*(HO + 1-butene) = 3.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K and atmospheric pressure of air (IUPAC, current recommendation).

(h) Relative to acetaldehyde

(i) Relative to ethene

(j) Relative to di-n-propyl ether

(k) Relative to isoprene

Preferred Values

Parameter	Value	*T*/K
k/ cm^3 $molecule^{-1}$ s^{-1}	2.6×10^{-11}	298
k/ cm^3 $molecule^{-1}$ s^{-1}	$6.8 \times 10^{-12} \exp(410/T)$	240-425
Reliability		
Δ log *k*	± 0.10	298
Δ E/R	± 60	

Comments on Preferred Values

The measurements of Kerr and Sheppard (1981), Semmes et al. (1985), Stemmler et al. (1997), Thévenet et al. (2000) and D'Anna et al. (2001) at 298 K are in very good agreement. The values reported by Audley et al. (1981) and Dóbé et al. (1989) are, respectively, ~ 40% lower and ~ 70% larger than the others. The preferred 298 K rate coefficient is derived from the mean of the room temperature rate coefficients of Kerr and Sheppard (1981), Semmes et al. (1985), Stemmler et al. (1997), Thévenet et al. (2000) and D'Anna et al. (2001). The temperature dependence is obtained from a fit to the data other than those Audley et al. (1981) and Dóbé et al. (1989). The relative rate coefficient of Audley et al. (1981) was not used in the evaluation, due to questions concerning the applicability of the experimental technique used (Semmes et al., 1985).

References

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