IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC14

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This data sheet last evaluated 16th October 2007 (with no revisions to preferred values).

HO + $CH_3CH_2CH_2CHO$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$5.7 \times 10^{-12} \exp[(411 \pm 164)/T]$	258-422	Semmes et al., 1985	FP-RF
$(2.06 \pm 0.30) \times 10^{-11}$	298		
$(2.88 \pm 0.26) \times 10^{-11}$	298	Albaladejo et al., 2002	PLP-LIF
Relative Rate Coefficients			
$(2.52 \pm 0.06) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981	RR (a)
$(2.45 \pm 0.15) \times 10^{-11}$	296 ± 2	Papagni et al., 2000	RR (b)
$(2.39 \pm 0.16) \times 10^{-11}$	298 ± 2	D'Anna et al., 2001	RR (c)

Comments

(a) HO radicals were generated by the photolysis of HONO in air and the concentrations of butanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + butanal)/k(HO + ethene) = 2.96 ± 0.07 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson, 1997).

(b) HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of butanal and methyl vinyl ketone (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + butanal)/k(HO + methyl vinyl ketone) = 1.20 ± 0.07 is placed on an absolute basis by use of a rate coefficient of k(HO + methyl vinyl ketone) = 2.04×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, 2007).

(c) HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of butanal and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + butanal)/k(HO + 1-butene) = 0.76 ± 0.05 is placed on an absolute basis by use of a rate coefficient of k(HO + 1-butene) = 3.14×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.0 \times 10^{-12} \exp(410/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-430 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta \log (E/R) = \pm 250$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the mean of the room temperature absolute rate coefficient of Semmes et al. (1985) and the relative rate coefficients of Kerr and Sheppard (1981), Papagni et al. (2000) and D'Anna et al. (2001). The temperature dependence is that measured by Semmes et al. (1985), with the pre-exponential factor being adjusted to fit the 298 K preferred value. The room temperature rate coefficient of Albaladejo et al. (2002) is in good agreement with the preferred value. The relative rate coefficient of Audley et al. (1981) has not been used in the evaluation because, while it is in good agreement with the preferred 298 K rate coefficient, the rate coefficients of Audley et al. (1981) for 2-methyl-1-propanal, 1-pentanal and 2,2-dimethyl-1-propanal are significantly lower than the values of Semmes et al. (1985) and Kerr and Sheppard (1981). At room temperature and below, the reaction is expected to proceed primarily by H-atom abstraction from the -CHO group.

References

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