

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC32

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This data sheet last evaluated: 18 December, 2007 (**with revision** of the preferred values).

HO + CH₃C(O)CH₂OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.0 \pm 0.3) \times 10^{-12}$	298	Dagaut et al., 1989	FP-RF
$(2.8 \pm 0.2) \times 10^{-12}$	~298	Chowdhury et al., 2002	PLP-LIF (a)
$2.15 \times 10^{-12} \exp[(305 \pm 10)/T]$	233-363	Dillon et al., 2006	PLP-LIF (b)
$(5.95 \pm 0.50) \times 10^{-12}$	298		
$(3.17 \pm 0.22) \times 10^{-12}$	298	Butkovskaya et al., 2006	DF-CIMS (c)
<i>Relative Rate Coefficients</i>			
$(2.52 \pm 0.27) \times 10^{-12}$	298	Orlando et al., 1999	RR (d,e)
$(3.52 \pm 0.32) \times 10^{-12}$	298	Orlando et al., 1999	RR (d,f)

Comments

- (a) HO radicals generated by the 193 nm photolysis of CH₃C(O)CH₂OH.
- (b) HO radicals were generated by the photolysis of HONO at 351 nm or by the 248 nm photolysis of O₃ in the presence of CH₄. Generation of HO radicals from the photolysis of O₃-CH₄ mixtures generally resulted in bi-exponential HO radical decays, attributed to HO radical regeneration from formation of H atoms from the reaction of O(¹D) atoms with CH₄ and their subsequent reaction with O₃. At 298 K, HO and DO radicals were also generated by the 248 nm photolysis of H₂O₂ and D₂O₂, respectively. The CH₃C(O)CH₂OH concentration immediately after passing through the reaction cell was monitored by UV absorption at 184.9 nm. Total pressure was varied over the range 50-200 Torr (67-267 mbar) with He or N₂ as the diluent gases, with the measured rate coefficients being independent of pressure over this range and of the HO radical generation method. At 298 K, the rate coefficient for the DO + CH₃C(O)CH₂OH reaction was within 10% of that for the HO radical reaction rate coefficient.
- (c) Experiments carried out at 200 Torr (267 mbar) pressure. The CH₃C(O)CH₂OH concentration immediately prior to entering the reaction cell was monitored by UV absorption at 254 nm. A rate coefficient of $k(\text{DO} + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}) = (4.08 \pm 0.31) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was also measured.
- (d) HO radicals were generated by the photolysis of methyl nitrite in synthetic air at 1 bar total pressure. Hydroxyacetone and methanol and ethanol (the reference compounds) were monitored by FTIR spectroscopy. The measured rate coefficient ratios $k(\text{HO} + \text{hydroxyacetone})/k(\text{HO} + \text{methanol}) = 2.8 \pm 0.3$ and $k(\text{HO} + \text{hydroxyacetone})/k(\text{HO} + \text{ethanol}) = 1.1 \pm 0.1$ are placed on an absolute basis using rate coefficients of $k(\text{HO} + \text{methanol}) = 9.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and

$k(\text{HO} + \text{ethanol}) = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, respectively (IUPAC, current recommendation).

(e) Relative to OH + methanol.

(f) Relative to OH + ethanol.

Preferred Values

$k = 4.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.6 \times 10^{-12} \exp(305/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230-370 K

Reliability

$\Delta \log k = \pm 0.25$ at 298 K.

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

Comments on Preferred Values

There is a factor of 2 discrepancy between the recent absolute rate study of Dillon et al. (2006) and the absolute and relative rate studies of Dagaut et al. (1989), Orlando et al. (1999), Chowdhury et al. (2002) and Butkovskaya et al. (2006), which are in reasonable agreement. At this time the reason(s) for this discrepancy are not understood, although it is possible that the Dagaut et al. (1989) and Chowdhury et al. (2002) studies measured erroneously low rate coefficients because of losses of $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ to the walls of the reaction vessel (Dillon et al., 2006). In the absence of data to confirm or disprove the most recent data of Dillon et al. (2006), the preferred 298 K rate coefficient is an average of the low and high measured values, with the uncertainty being sufficient to encompass both. The temperature dependence of Dillon et al. (2006) is accepted, and the pre-exponential factor adjusted to fit the 298 K preferred value.

References

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