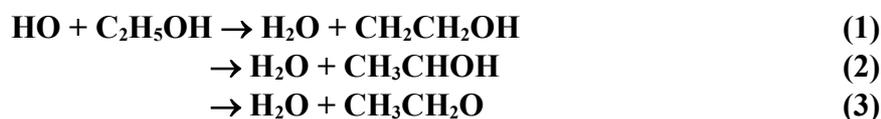


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC24

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet last evaluated June 2009 (with no revisions of the preferred values).



$$\Delta H^\circ(1) = -67 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -95.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -59.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.25 \times 10^{-11} \exp[-(360 \pm 52)/T]$	255-459	Greenhill and O'Grady, 1986	FP-RA
$(3.40 \pm 0.17) \times 10^{-12}$	293		
$7.4 \times 10^{-12} \exp[-(240 \pm 110)/T]$	240-440	Wallington and Kurylo, 1987	FP-RF
$(3.33 \pm 0.23) \times 10^{-12}$	296		
$(3.26 \pm 0.14) \times 10^{-12}$	293	Hess and Tully, 1988	PLP-LIF (a,b)
$(3.33 \pm 0.14) \times 10^{-12}$	326.5		
$(3.63 \pm 0.15) \times 10^{-12}$	380		
$(3.94 \pm 0.16) \times 10^{-12}$	441		
$(3.32 \pm 0.16) \times 10^{-12}$	295	Hess and Tully, 1988	PLP-LIF (b,c)
$(5.47 \pm 0.34) \times 10^{-12}$	599		
$(3.04 \pm 0.25) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
$k_2 + k_3 = (8.80 \pm 1.32) \times 10^{-12}$	1204 ± 16	Bott and Cohen, 1991	SH-RA (d)
$4.3 \times 10^{-12} \exp[-(85 \pm 35)/T]$	227-360	Jiménez et al., 2003	PLP-LIF
$(3.1 \pm 0.4) \times 10^{-12}$	298		
$4.0 \times 10^{-12} \exp[-(42 \pm 10)/T]$	216-368	Dillon et al., 2005	PLP-LIF (e)
$(3.35 \pm 0.17) \times 10^{-12}$	298 ± 2		
$5.27 \times 10^{-18} T^2 \exp[(557 \pm 20)/T]$	298-500	Carr et al., 2008	PLP-LIF (f)
3.03×10^{-12}	298		
$5.87 \times 10^{-18} T^2 \exp[(515 \pm 21)/T]$	298-498	Carr et al., 2008	PLP-LIF (g)
2.94×10^{-12}	298		
<i>Relative Rate Coefficients</i>			
$(3.22 \pm 0.49) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (h)
$(3.64 \pm 0.11) \times 10^{-12}$	298 ± 4	Picquet et al., 1998	RR (i)
$(2.79 \pm 0.28) \times 10^{-12}$	298 ± 2	Oh and Andino, 2001	RR (h)
$(2.72 \pm 0.25) \times 10^{-12}$	298 ± 2	Oh and Andino, 2001	RR (j)
$(3.39 \pm 0.24) \times 10^{-12}$	296 ± 2	Sørensen et al., 2002	RR (k,l)
$(3.36 \pm 0.35) \times 10^{-12}$	296 ± 2	Sørensen et al., 2002	RR (k,m)
$(3.37 \pm 0.25) \times 10^{-12}$	295 ± 2	Wu et al., 2003	RR (n)

Comments

- (a) Reaction of H¹⁶O radicals.
- (b) Thermal decomposition of the H¹⁶OCH₂CH₂ radical formed by H-atom abstraction from the CH₃ group to regenerate H¹⁶O radicals occurs at temperatures >500 K, and hence the H¹⁶O rate coefficient data do not yield the rate coefficient $k = (k_1 + k_2 + k_3)$ above ~500 K. Since thermal decomposition of the H¹⁶OCH₂CH₂ radical does not lead to regeneration of the H¹⁸O radical, the H¹⁸O rate coefficient data yield the overall reaction rate coefficient, $k = (k_1 + k_2 + k_3)$.
- (c) Rate coefficients for reaction of the H¹⁸O radical. H¹⁸O radicals were generated from pulsed laser photolysis of H₂¹⁸O, with H¹⁸O radicals being detected by LIF.
- (d) HO radicals were generated by the thermal decomposition of *t*-butyl hydroperoxide in a shock tube, with detection by resonance absorption at 309 nm. The measured rate coefficient corresponds to $(k_2 + k_3)$ because of the rapid thermal decomposition of the CH₂CH₂OH radical formed in reaction channel (1) [this is the same radical as formed from the addition of HO radicals to ethene].
- (e) The ethanol concentrations in the reactant gas stream were measured by optical absorption at 185 nm in a cell downstream of the reaction cell.
- (f) HO radicals were generated by the photolysis of *t*-butyl hydroperoxide at 248 nm. Total pressures were in the range 25-198.5 Torr (33-265 mbar) of He diluent. The cited rate expression is from a weighted fit using the statistical errors only; inclusion of systematic uncertainties results in the rate expression $k = 5.7 \times 10^{-18} T^2 \exp[(530 \pm 220)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Carr et al., 2008).
- (g) HO radicals were generated by the photolysis of CH₃C(O)CH₃-O₂ mixtures at 248 nm. Total pressures were in the range 25-50 Torr (33-67 mbar) of He diluent. The cited rate expression is from a weighted fit using the statistical errors only; inclusion of systematic uncertainties results in the rate expression $k = 6.2 \times 10^{-18} T^2 \exp[(500 \pm 200)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Carr et al., 2008).
- (h) HO radicals were generated by photolysis of CH₃ONO in air. The ethanol and cyclohexane (the reference organic) concentrations were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).
- (i) HO radicals were generated by the photolysis of H₂O₂ in air at 254 and 310 nm. The concentrations of ethanol and *n*-hexane (the reference compound) were measured by GC. The measured rate coefficient ratio, $k(\text{HO} + \text{ethanol})/k(\text{HO} + \textit{n}\text{-hexane})$, is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \textit{n}\text{-hexane}) = 5.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).
- (j) HO radicals were generated by photolysis of CH₃ONO in air. The ethanol and *p*-xylene (the reference organic) concentrations were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{ethanol})/k(\text{HO} + \textit{p}\text{-xylene}) = 0.19 \pm 0.01$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{p}\text{-xylene}) = 1.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al., 2002).
- (k) HO radicals were generated by the photolysis of CH₃ONO in air at 1.0 bar (750 Torr). The concentrations of ethanol and acetylene or ethene (the reference compounds) were measured by in situ FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{ethanol})/k(\text{HO} + \text{acetylene}) = 4.35 \pm 0.30$ and $k(\text{HO} + \text{ethanol})/k(\text{HO} + \text{ethene}) = 0.39 \pm 0.04$ are placed on an absolute basis using rate coefficients of $k(\text{HO} + \text{acetylene}) = 7.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 750 Torr pressure of air or O₂ and $296 \pm 2 \text{ K}$ (Sørensen et al., 2003) and $k(\text{HO} + \text{ethene}) = 8.61 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K and atmospheric pressure of air (Atkinson, 1997). No effect of the presence of NaCl or NH₄NO₃ aerosol was observed.
- (l) Relative to acetylene.
- (m) Relative to ethene.
- (n) HO radicals were generated by the photolysis of H₂O₂ in 1 atmosphere of air at 254 nm. The concentrations of ethanol and propane (the reference compound) were measured by GC. The measured rate coefficient ratio, $k(\text{HO} + \text{ethanol})/k(\text{HO} + \text{propane})$, 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

$k = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.0 \times 10^{-12} \exp(20/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 210-300 K.

$k_1/k = 0.05$ at 298 K.

$k_3/k = 0.05$ at 298 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

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

$\Delta k_1/k = {}^{+0.10}_{-0.05}$ at 298 K.

$\Delta k_3/k = {}^{+0.10}_{-0.05}$ at 298 K.

Comments on Preferred Values

Room temperature rate coefficients determined from absolute and relative rate studies carried out since ~1985 are in good agreement. The preferred rate coefficient is derived from fitting the H¹⁸O and (for temperatures <500 K) the H¹⁶O rate coefficients of Hess and Tully (1988) and the absolute rate constants determined by Wallington and Kurylo (1987), Jiménez et al. (2003) and Dillon et al. (2005) to the expression $k = C T^2 \exp(-D/T)$. This results in $k = 6.70 \times 10^{-18} T^2 \exp(511/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 216-599 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$ is centered at 245 K and is derived from this three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$. Note that the Arrhenius expression should not be used outside of the stated temperature range (210-300 K); rather the three-parameter expression $k = 6.70 \times 10^{-18} T^2 \exp(511/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ should be employed. The rate coefficient calculated from the preferred Arrhenius expression at 255 K is 14% higher than the lowest temperature rate coefficient reported by Greenhill and O'Grady (1986). The preferred 298 K rate coefficient is in good agreement with the absolute and relative rate coefficients of Nelson et al. (1990), Picquet et al. (1998), Sørensen et al. (2002), Wu et al. (2003) and Carr et al. (2008), and is ~15% higher than the relative rate data of Oh and Andino (2001). The rate coefficient measured by Bott and Cohen (1991) at 1204 K, and ascribed to $(k_2 + k_3)$, is consistent with the value of $(k_1 + k_2 + k_3)$ calculated from the recommended three parameter expression and with the rate coefficient k_1 at 1204 K estimated using the procedure of Kwok and Atkinson (1995).

Meier et al. (1985) determined that at room temperature the reaction proceeds mainly ($75 \pm 15\%$) via formation of the CH₃CHOH radical, consistent with the thermochemistry of the reaction steps. The kinetic data of Hess and Tully (1988) for the reactions of the H¹⁶O and H¹⁸O radicals with ethanol indicate that channel (1) accounts for ~15% of the overall reaction at 600 K, in agreement with the calculated value of 17% from the estimation procedure of Kwok and Atkinson (1995). This agreement allows a rate coefficient ratio of $k_1/k = 0.05$ at 298 K to be estimated. Assuming that H-atom abstraction from the -OH group in ethanol [channel (3)] has a similar rate coefficient to the analogous channel for methanol (IUPAC, current recommendation) allows $k_3/k = 0.05$ at 298 K to be estimated. The resulting value of $k_2/k = 0.90$ at 298 K is just consistent with the product data of Meier et al. (1985).

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