IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC69

This data sheet last evaluated: June 2009.

HO + $(CH_3)_2CHCH_2OH$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.1\pm0.9) \times 10^{-12} \exp[(352 \pm 82)/T]$	241-370	Mellouki et al., 2004	PLP-LIF (a)
$(9.2 \pm 0.4) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(8.8 \pm 0.3) \times 10^{-12}$	295 ± 2	Wu et al., 2003	RR (b, d)
$(9.2 \pm 0.4) \times 10^{-12}$	295 ± 2	Wu et al., 2003	RR (b, e)
$(8.5 \pm 0.1) \times 10^{-12}$	298 ± 2	Mellouki et al., 2004	RR (c, f)
$(8.8 \pm 0.3) \times 10^{-12}$	298 ± 2	Mellouki et al., 2004	RR (c, g)

Comments

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

(b) HO radicals were generated by the photolysis of H_2O_2 in 1 atmosphere of air at 254 nm. Experiments were carried out in a ~100 liter Teflon chamber, and the concentrations of 2-methyl-1-propanol (isobutyl alcohol), propane and cyclohexane (the reference organics) were measured by GC-FID. The measured rate coefficient ratios of k(HO + $(CH_3)_2CHCH_2OH$)/k(HO + propane) and k(HO + $(CH_3)_2CHCH_2OH$)/k(HO + cyclohexane) are placed on an absolute basis using k(HO + propane) = 1.05×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) and k(HO + cyclohexane) = 6.9×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K (Calvert et al., 2008).

(c) HO radicals were generated by the photolysis of H_2O_2 in 1 atmosphere of air at 254 nm. Experiments were carried out in a ~120 liter Teflon chamber, and the concentrations of 2-methyl-1-propanol (isobutyl alcohol), 1-butanol and 1,3-dioxolane (the reference organics) were measured by GC-FID. The measured rate coefficient ratios of k(HO + $(CH_3)_2CHCH_2OH$)/k(HO + 1-butanol) = 1.00 ± 0.01 and k(HO + $(CH_3)_2CHCH_2OH$)/k(HO + 1,3-dioxolane) = 0.88 ± 0.03 are placed on an absolute basis using k(HO + 1-butanol) = 8.5×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson et al., 2006) and k(HO + 1,3-dioxolane) = 1.0×10^{-11} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2008).

(d) Relative to HO + propane

(e) Relative to HO + cyclohexane

(f) Relative to HO + 1-butanol

(g) Relative to HO + 1,3-dioxolane

Preferred Values

Parameter	Value	*T*/K
k/cm^3 molecule^{-1} s^{-1}	8.9×10^{-12}	298
k/cm^3 molecule^{-1} s^{-1}	2.73×10^{-12} exp(352/T)	240-370
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 120	

Comments on Preferred Values

The 298 K rate coefficients values from the absolute and relative studies of Mellouki et al. (2004) are in very good agreement with those from the relative determination of Wu et al. (2003). The preferred rate coefficient value at 298 K is derived from the average of the measurements reported in these two studies. The absolute rate study of Mellouki et al. (2004), the sole temperature-dependence study, combined with the preferred 298 K is used to derive the pre-exponential factor.

The reaction of OH with 2-methyl-1-propanol is expected to proceed via H-atom abstraction from –CH_2– and >CH– groups with a lower contribution from the CH_3–groups.

$OH + (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2CHCH_2O$ (a)

$OH + (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2CHCHOH$ (b)

$OH + (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2CCH_2OH$ (c)

$OH + (CH_3)_2CHCH_2OH \rightarrow H_2O + CH_2CH(CH_3)CH_2OH$ (d)

The α-hydroxy alkyl radical formed by H-atom abstraction from –CH_2– group (channel b) reacts with O_2 to form 2-methyl propanal ($(CH_3)_2CHCHO$). The hydroxyl alkyl radicals formed in channels (c) and (d) will add O_2 then react with NO to give the alkoxy radicals $(CH_3)_2C(O)CH_2OH$ and $OCH_2CH(CH_3)CH_2OH$. $(CH_3)_2C(O)CH_2OH$ radicals decompose to give acetone and formaldehyde. $OCH_2CH(CH_3)CH_2OH$ radicals react with O_2 to give $HC(O)CH(CH_3)CH_2OH$ and decompose to give $2HCHO + CH_3CHO$.

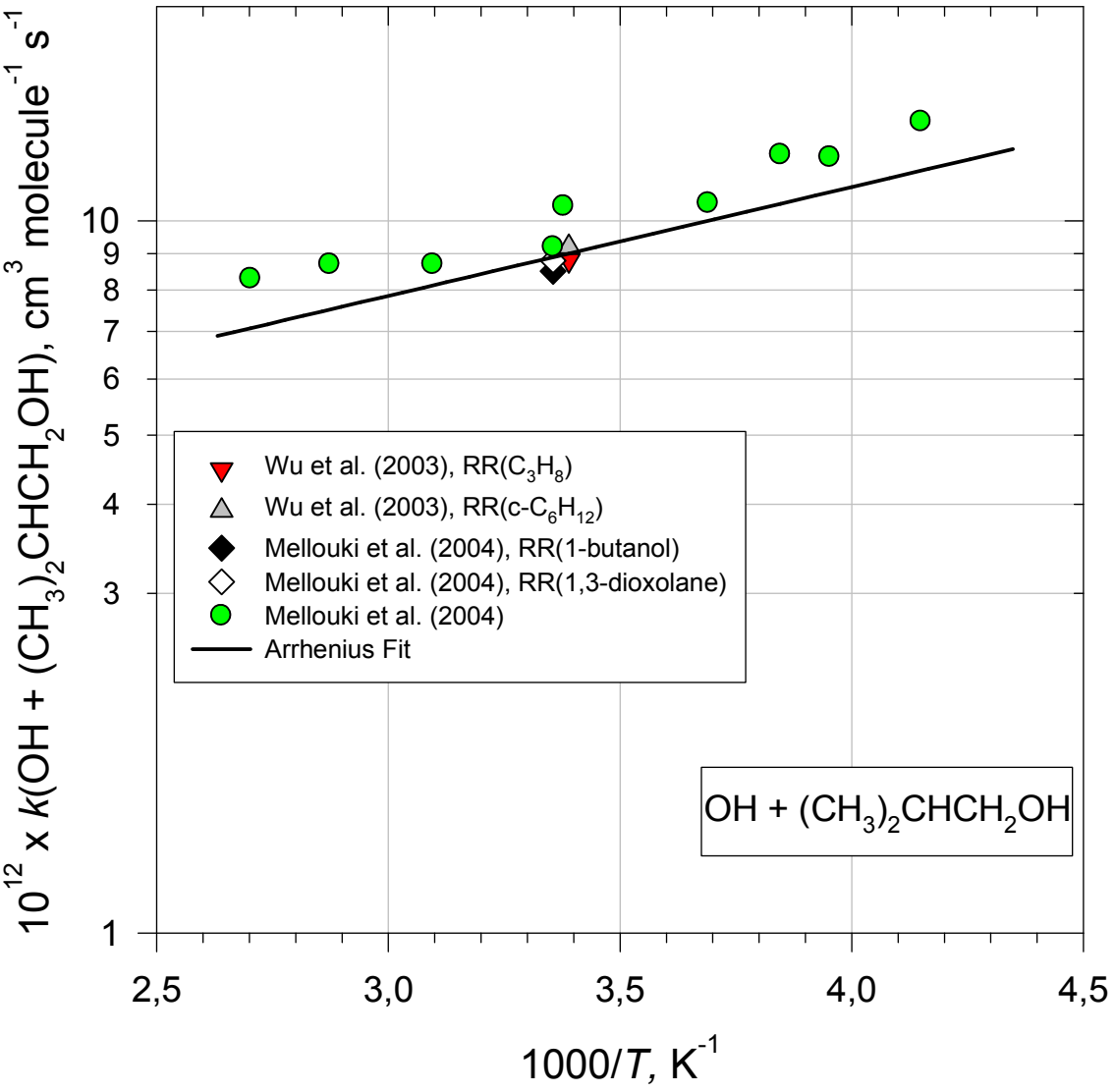
References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.

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

Mellouki, A., Oussar, F., Lun, X., and Chakir, A.: Phys. Chem. Chem. Phys., 6, 2951, 2004.

Wu, H., Mu, Y., Zhang, X., and Jiang, G.: Int. J. Chem. Kinet., 35, 81, 2003.


10^{12} x k(OH + $(CH_3)_2CHCH_2OH$), cm^3 molecule^{-1} s^{-1}
10
9
8
7
6
5
4
3
1
2,5
3,0
3,5
4,0
4,5
1000/T, K^{-1}
Wu et al. (2003), RR(C_3H_8)
Wu et al. (2003), RR(c-C_6H_{12})
Mellouki et al. (2004), RR(1-butanol)
Mellouki et al. (2004), RR(1,3-dioxolane)
Mellouki et al. (2004)
Arrhenius Fit
OH + $(CH_3)_2CHCH_2OH$