

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_44

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (8.8 \pm 1.0) \times 10^{-13}$	298	Jenkin and Hayman, 1995	MM-UVA (a,b)
$k_{\text{obs}} = (7.9 \pm 0.7) \times 10^{-13}$	296		PLP-UVA (a,b)
$(6.79 \pm 0.41) \times 10^{-13}$	303	Boyd and Lesclaux, 1997	PLP-UVA (a,c)
$7.7 \times 10^{-15} \exp[(1330 \pm 350)/T]$	303-421		
<i>Branching Ratios</i>			
$k_1/k_2 = 4.0 \times 10^4 \exp[(3600 \pm 100)/T]$	303-421	Boyd and Lesclaux, 1997	PLP-UVA (a,c)

Comments

- (a) k is defined by $-d[\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3]/dt = 2k [\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3]^2$. k_{obs} denotes an upper limit rate coefficient derived from an experimentally observed decay without correction for probable secondary removal of $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$.
- (b) $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$ generated from the photolysis of H_2O_2 -but-2-ene- O_2 - N_2 mixtures at 1 bar (750 Torr), at 254 nm (in the MM experiments) or 248 nm (in the PLP experiments). Absorption spectrum characterised over the wavelength range 210-300 nm. k_{obs} determined from transient decay traces recorded at 250 nm, which were found to obey second order kinetics.
- (c) $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$ generated from the 248 nm photolysis of H_2O_2 -but-2-ene- O_2 - N_2 mixtures at 1013 mbar (760 Torr). The kinetics and branching ratios were determined from simulation of the transient decay traces recorded at 220 nm and 270 (or 280) nm. Quantification of the branching ratio was found to be sensitive to the deviation from second order kinetics and to a distortion to the trace at 220 nm, which results from an additional absorption due to HO_2 formation from propagating channel (1). No detectable deviation from second order kinetics was observed at 303 K, consistent with $k_1/k_2 < 0.3$; but increasing with temperature such that $k_1/k_2 = (0.88 \pm 0.10)$ at 421 K. Expression for k_1/k_2 determined from higher temperature data, and extrapolated to allow analysis of the data obtained at 303 K.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	6.7×10^{-13}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.7 \times 10^{-15} \exp(1330/T)$	298 - 420
k_1/k	0.18	298
k_2/k	0.82	298
k_1/k	$1/[1 + 2.5 \times 10^{-5} \exp(3600/T)]$	298 - 420
k_2/k	$1 - (k_1/k)$	298 - 420
<i>Reliability</i>		
$\Delta \log k$	± 0.2	298 - 400
$\Delta E/R$	$\pm 300 \text{ K}$	
$\Delta k_1/k$	± 0.15	298
$\Delta k_2/k$	± 0.15	298
$\Delta(E_1/R - E/R)$	$\pm 500 \text{ K}$	

Comments on Preferred Values

The preferred values of k and the branching ratios are based on the temperature dependence expressions of Boyd and Lesclaux (1997). The room temperature values of k_{obs} reported by Jenkin and Hayman (1995) also agree well with the preferred value at 298 K, when corrected for secondary removal of $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$ via reaction with HO_2 , using the conventional expression, $k_{\text{obs}} = (1 + (k_1/k))k$. Additional studies are required to confirm the magnitude of the temperature dependence of the reaction.

The API-MS study of Tuazon et al. (1998) reported formation of the hydroxycarbonyl, $\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{O})\text{CH}_3$, and the dihydroxyalkane, $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$, during the HO initiated oxidation of *cis*-but-2-ene and *trans*-but-2-ene in the absence of NO_x (at 297 K and 986 mbar) attributed to the operation of reaction channel (2). The formation of the hydroxyhydroperoxide, $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$, was also observed and attributed to the secondary reaction of $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$ with HO_2 , formed from the subsequent chemistry of $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O})\text{CH}_3$ produced in reaction channel (1). Further quantitative product studies are required to confirm, and reduce the uncertainties on, the preferred branching ratios.

References

- Boyd, A.A. and Lesclaux, R.: *Int J Chem Kinet.*, 29, 323, 1997.
 Jenkin, M. E. and Hayman, G. D.: *J. Chem. Soc. Faraday Trans.*, 91, 1911, 1995.
 Tuazon, E.C., Aschmann, S.M., Arey, J. and Atkinson, R.: *Environ. Sci. Technol.*, 32, 2106, 1998.

