

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_46

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This data sheet last evaluated: June 2011; last change in preferred values: June 2011.



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>			
$k_{\text{obs}} = (7.8 \pm 1.5) \times 10^{-12}$	298	Langer et al., 1994	PR-UVA (a,b)
$(3.88 \pm 0.16) \times 10^{-12}$	306	Boyd et al., 1996	FP-UVA (a,c)
$1.4 \times 10^{-14} \exp[(1740 \pm 150)/T]$	306-398		
$k_{\text{obs}} = (4.4 \pm 0.7) \times 10^{-12}$	298	Chakir et al., 2004	MM-UVA (a,d)
2.8×10^{-12}	298		
$k_{\text{obs}} = 4.1 \times 10^{-15} \exp[(2086 \pm 120)/T]$	298-349		
$4.8 \times 10^{-15} \exp[(1903 \pm 116)/T]$	298-349		
<i>Branching Ratios</i>			
$k_1/k = (0.59 \pm 0.15)$	306-398	Boyd et al., 1996	FP-UVA (c)
$k_1/k = (0.60 \pm 0.07)$	296		UVP-FTIR (e)

Comments

- k is defined by $-d[(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2]/dt = 2k [(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2]^2$. k_{obs} denotes an upper limit rate coefficient derived from an experimentally observed decay without correction for probable secondary removal of $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$.
- $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$ generated from the pulsed radiolysis of SF_6/t -butanol/ O_2 mixtures at 1 bar. Absorption spectrum characterised over the wavelength range 220-320 nm, maximising at about 240-250 nm; $\sigma_{250\text{nm}} = 3.39 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. k_{obs} determined from transient decay traces recorded at 240 nm, which were found to obey second order kinetics.
- $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$ generated from the flash photolysis of Cl_2-t -butanol- O_2 - N_2 mixtures at 1013 mbar (760 Torr). Absorption spectrum characterised over the wavelength range 210-290 nm, maximising at 250 nm; $\sigma_{250\text{nm}} = 3.98 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. Kinetics experiments were performed in sets, in which CH_3OH also added in known amounts to provide a primary source of HO_2 and a range in initial $[(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2]/[\text{HO}_2]$. k and k_1/k were determined from simulation of the transient decay traces recorded at 260 nm and 220 nm (where HO_2 also absorbs significantly) in each set of experiments, using a chemical mechanism informed by the companion FTIR product study (see note (e)). This involved an iterative procedure in which the rate coefficient for the reaction of HO_2 with $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$ was also determined.
- $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$ generated from the modulated photolysis of Cl_2-t -butanol- O_2 - N_2 mixtures, using blacklights. Absorption spectrum of $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$ characterised over

the range 210-270 nm from the initial increase in absorbance in light-on phase of the modulated waveform. The maximum was observed at about 255-260 nm; $\sigma_{260\text{nm}} = 3.70 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. k_{obs} was determined from analysis of the steady state absorption due to $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$ in the latter part of the light-on phase of the modulated waveform, following correction for the steady accumulation of stable absorbing products, the absorption spectra of which were also reported. k determined from the expression $k = k_{\text{obs}}/(1+(k_1/k))$, using the values of k_1/k reported by Boyd et al. (1996). Confirmatory simulations of the modulated waveforms carried out using a detailed reaction scheme.

- (e) UV irradiation of Cl_2 -*t*-butanol- O_2 - N_2 mixtures in a smog chamber fitted with an FTIR detection system, at a total pressure of 930 mbar. HCHO and acetone identified as products, with their respective yields quantified as $(38 \pm 4) \%$ and $(39 \pm 4) \%$ using calibrated spectra. Residual absorption bands observed, which were consistent with formation of $(\text{CH}_3)_2\text{C}(\text{OH})\text{CHO}$, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{OH}$ and $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{OOH}$, although this was not confirmed due to unavailability of these reference compounds. Failure to detect acetone formation in additional experiments in the absence of O_2 indicated that $> 98 \%$ of the $\text{Cl} + t$ -butanol reaction proceeds via abstraction of H from the CH_3 - groups, to form $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2$. With the aid of simulations of the system, informed by the companion flash photolysis study (see note (c)), the yield of acetone in the presence of O_2 was used to determine k_1/k .

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4.8×10^{-12}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.4 \times 10^{-14} \exp(1740/T)$	298 - 400
k_1/k	0.6	298 - 400
k_2/k	0.4	298 - 400
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298 - 400
$\Delta E/R$	$\pm 300 \text{ K}$	
$\Delta k_1/k$	± 0.2	298 - 400
$\Delta k_2/k$	± 0.2	298 - 400

Comments on Preferred Values

The preferred values of k are based on the temperature dependence expression of Boyd et al. (1996), which is the most direct study of the reaction kinetics and absorption spectrum. The 298 K value of k_{obs} reported by Langer et al. (1994) is consistent with this recommendation, given the secondary removal of $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$ via reaction with HO_2 , and also possibly by reaction with $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2$ under the conditions employed (as discussed by Langer et al., 1994). The temperature dependence of k reported by Chakir et al. (2004) is in good agreement with that of Boyd et al. (1996), but the values of k are lower by almost a factor of 2 over the measured temperature range. The uncertainty assigned to the preferred values therefore encompasses the results of Chakir et al. (2004).

The preferred values of k_1/k and k_2/k are based those reported by Boyd et al. (1996). At close to room temperature, the reported formation of acetone and HCHO in the FTIR study and the formation of secondary HO₂ in the flash photolysis study, provided direct measurements of k_1/k which are in good agreement. At higher temperatures, the flash photolysis data of Boyd et al. (1996) suggest little change in k_1/k , although confirmatory product studies would be valuable.

References

Boyd, A.A., Lesclaux, R., Jenkin, M.E. and Wallington, T.J.: J. Phys. Chem., 100, 6594, 1996.

Chakir, A., Ganne, J.P., Roth, E., Brion, J. and Daumont, D.: Phys. Chem. Chem. Phys., 6, 3389, 2004.

Langer, S., Ljungström, E., Sehested, J. and Nielsen, O.J.: Chem. Phys. Lett., 226, 165, 1994.

