

Task Group on Atmospheric Chemical Kinetic Data Evaluation– Data Sheet HO_x_VOC98

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The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>), 2017.

This datasheet last evaluated: Nov. 2017; last change in preferred values: Nov. 2017



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$(9.4\text{-}11.9) \times 10^{-12}$	298	Wu et al., 2017	RR (a)

Comments

- (a) Experiments were conducted at 1 bar of air in a ≈ 2 L cylindrical, quartz flow-reactor with residence times of 100 to 400s. HO was generated by the broad-band (290-400 nm) photolysis of H₂O₂. CH₃C(O)OOH and the reference gases (toluene and *m*-xylene) were detected by HPLC and GC, respectively. Rate coefficient ratios of $k(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OH}) / k(\text{OH} + \text{toluene}) = 1.65 \pm 0.11$ and $k(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OH}) / k(\text{OH} + \textit{m}\text{-xylene}) = 0.43 \pm 0.03$ were placed on an absolute basis using $k(\text{OH} + \text{toluene}) = 5.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{OH} + \textit{m}\text{-xylene}) = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Corrections were applied for the loss of CH₃C(O)OOH by photolysis and also due to its reformation via the reaction of HO₂ (formed in OH + H₂O₂) with CH₃C(O)O₂ radicals (formed in (1)). The authors report an uncorrected value of $k = (9.4 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a corrected value of $k = (11.9 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.1×10^{-11}	298
k_1/k	0.5	298
k_2/k	0.5	298
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298
$\Delta(k_1/k)$	0.35	298
$\Delta(k_2/k)$	0.35	298

Comments on Preferred Values

There is only one experimental study of the rate coefficient of this reaction (Wu et al., 2017). The $\text{CH}_3\text{C}(\text{O})\text{OOH}$ depletion factor required correction for loss by photolysis and for its reformation in secondary reactions (see comment (a)). The latter required numerical simulation of the complex chemistry involving self and cross-reactions of the various peroxy radicals formed and also the branching ratio, (k_1/k) . The authors chose a value of $(k_1/k) = 0.46$ and cite a theoretical study (Rypkema and Francisco, 2013), which however only reported relative A-factors for the two reaction pathways and stated that reaction flux through the two channels are comparable as barriers are also calculated to be similar. The uncertainty we associate with $k(298\text{ K})$ reflects the extensive corrections necessary and the fact that the branching ratio has never been determined experimentally.

Wu et al., (2017) identified HCHO and $\text{HC}(\text{O})\text{OH}$ as the major end-products of the reaction in the absence of NO_x . There are complex routes for formation and loss of HCHO and $\text{HC}(\text{O})\text{OH}$ in these experiments and we therefore adopt the theoretical result (Rypkema and Francisco, 2013) of “comparable importance” for the two reactions and increase the uncertainty appropriately. In air and in the presence of NO, The dominant fate of $\text{CH}_2\text{C}(\text{O})\text{OOH}$ formed in the abstraction of the methyl-hydrogen involves formation and reaction of peroxy and alkoxy radicals en route to CO_2 and the CH_2OH radical (Rypkema and Francisco, 2013).



Further studies of the rate coefficient and branching ratio are required to reduce uncertainty for this reaction.

References

- Rypkema, H. A., and Francisco, J. S., *J. Phys. Chem. A*, 117, 14151-14162, 2013.
Wu, H., Wang, Y., Li, H., Huang, L., Huang, D., Shen, H., Xing, Y., and Chen, Z., *Atmos. Env.*, 164, 61-70, 2017.