

## Task Group on Atmospheric Chemical Kinetic Data Evaluation– Data Sheet HO<sub>x</sub>\_VOC98

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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>			
$< 4 \times 10^{-14}$	298	Berasategui et al., 2020	PLP-LIF (a)
$< 4 \times 10^{-14}$	298-353		
<i>Relative Rate Coefficients</i>			
$(9.4-11.9) \times 10^{-12}$	298	Wu et al., 2017	RR (a)

### Comments

- (a) HO was generated by the 248 nm photolysis of CH<sub>3</sub>C(O)OOH samples containing ~30% CH<sub>3</sub>C(O)OH impurity. On-line FTIR was used to measure the CH<sub>3</sub>C(O)OOH and CH<sub>3</sub>C(O)OH concentrations. Once corrected for the reaction with CH<sub>3</sub>C(O)OH and taking into account potential reaction of HO with CH<sub>3</sub> radicals formed in the photolysis of CH<sub>3</sub>C(O)OOH, the HO decay coefficients indicated that the reaction with CH<sub>3</sub>C(O)OOH is very slow at all temperatures covered. Thus, the authors present only an upper limit to  $k$ .
- (b) Experiments were conducted at 1 bar of air in a  $\approx 2$  L cylindrical, quartz flow-reactor with residence times of 100 to 400s. HO was generated by the broad-band (290-400 nm) photolysis of H<sub>2</sub>O<sub>2</sub>. CH<sub>3</sub>C(O)OOH and the reference gases (toluene and *m*-xylene) were detected by HPLC and GC, respectively. Rate coefficient ratios of  $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{OH}) / k(\text{HO} + \text{toluene}) = 1.65 \pm 0.11$  and  $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{OH}) / k(\text{HO} + m\text{-xylene}) = 0.43 \pm 0.03$  were placed on an absolute basis using  $k(\text{HO} + \text{toluene}) = 5.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{HO} + m\text{-xylene}) = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Corrections were applied for the loss of CH<sub>3</sub>C(O)OOH by photolysis and also due to its reformation via the reaction of HO<sub>2</sub> (formed in HO + H<sub>2</sub>O<sub>2</sub>) with CH<sub>3</sub>C(O)O<sub>2</sub> 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

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3 \times 10^{-14}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.16 \times 10^{-46} T^{10.90} \exp(3447/T)$	200-450
$k_1 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.43 \times 10^{-43} T^{9.87} \exp(3287/T)$	200-450
$k_2 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$9.65 \times 10^{-47} T^{11.10} \exp(3000/T)$	200-450
$k_1/k$	0.78	298
$k_2/k$	0.22	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.3$	298
$\Delta(k_1/k)$	$\pm 0.35$	298
$\Delta(k_2/k)$	$\pm 0.35$	298

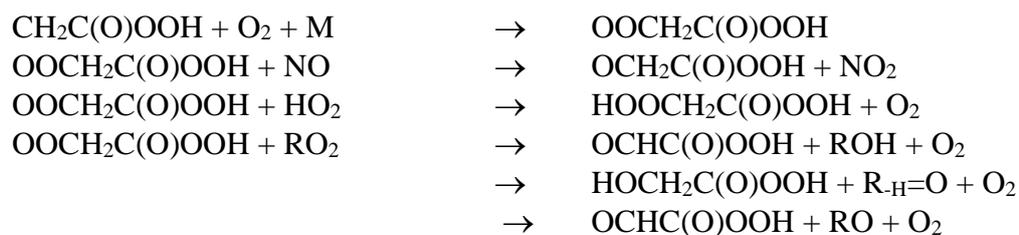
### *Comments on Preferred Values*

The two experimental studies of the reaction between HO and  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  report room temperature rate coefficients that disagree by a factor of  $\sim 250$ . In their absolute study, Berasategui et al (2020) saw no evidence for reaction between HO and  $\text{CH}_3\text{C}(\text{O})\text{OOH}$ ; experiments with DO ruling out possible radical reformation as the cause of the low loss rates of HO. The reported upper limit to  $k$  was consistent with high-level quantum chemical calculations ( $k = 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K) which showed that the reaction proceeds via a relatively weakly bonded and short-lived pre-reaction complex in which H-abstraction occurs only slowly due to a high barrier and low tunnelling probabilities. The theoretical rate coefficients reported were  $k = 3.16 \times 10^{-46} T^{10.90} \exp(3447/T)$  with  $k_{1a} = 1.43 \times 10^{-43} T^{9.87} \exp(3287/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{1b} = 9.65 \times 10^{-47} T^{11.10} \exp(3000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

It is difficult to reconcile the greatly divergent results of the two experimental studies. In the relative-rate studies of 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 re-formation in secondary reactions. 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). In their theoretical study, Berasategui et al (2020) also indicate that both reaction pathways contribute with  $k_1/k = 0.78$  and  $k_2/k = 0.22$  at 298 K. Abstraction of the peracetic H-atom (reaction 1) dominated across the temperature range 200-450 K. The use of a branching ratio that is potentially wrong by 50% cannot explain the difference in rate coefficients obtained in the two studies. Berasategui et al (2020) do however note that, in relative rate experiments carried out in their laboratory, large and variable wall losses of  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  precluded measurement of an accurate value of  $k$ .

We thus base our recommendation of both rate coefficient and branching ratio on the combined absolute PLP-LIF and theoretical study of Berasategui et al (2020); the factor two uncertainty in  $k$  is based on assessment of the accuracy of the theoretical calculations.

In air, the minor  $\text{CH}_2\text{C}(\text{O})\text{OOH}$  product of reaction 2 is expected to add  $\text{O}_2$ , forming a peracetic acid peroxy radical,  $\text{OOCH}_2\text{C}(\text{O})\text{OOH}$ , which will undergo reactions with NO,  $\text{RO}_2$  and  $\text{HO}_2$ .



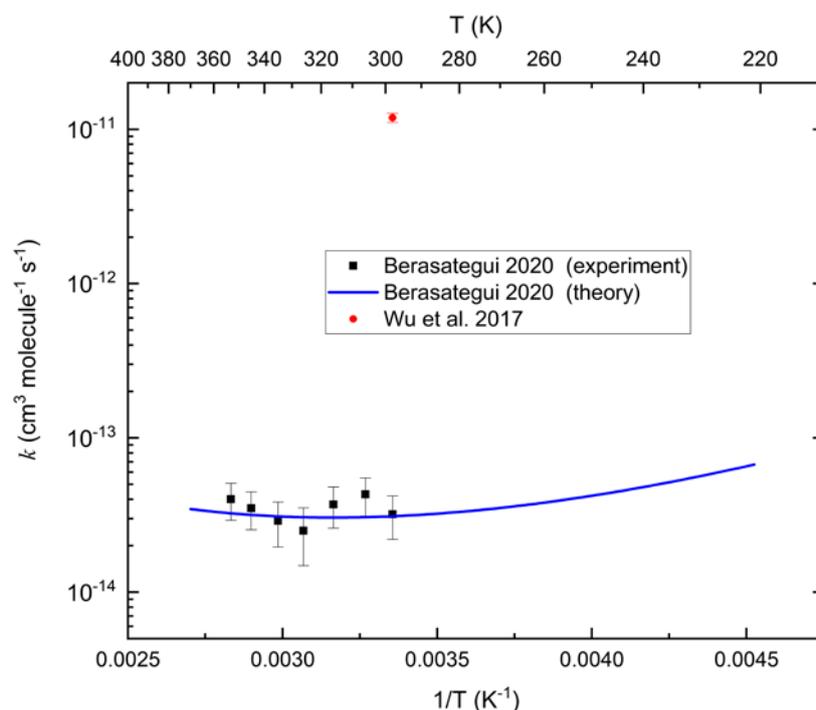
The oxy radical product,  $\text{OCH}_2\text{C}(\text{O})\text{OOH}$ , formed from the propagating channels of these reactions will quickly decompose to  $\text{HCHO}$ ,  $\text{CO}_2$  and  $\text{HO}$  (Vereecken and Peeters, 2009).



Further experimental work on the  $\text{HO} + \text{CH}_3\text{C}(\text{O})\text{OOH}$  reaction is required to reduce uncertainty associated with both the rate coefficient and product formation in this reaction and confirm that  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  has an atmospheric lifetime with respect to reaction with  $\text{HO}$  on the order of a year.

### References

- Berasategui, M., Amedro, D., Vereecken, L., Lelieveld, J., and Crowley, J. N., *Atmos. Chem. Phys. Discuss.*, 2020, 1-29, 2020.  
 Rypkema, H. A., and Francisco, J. S., *J. Phys. Chem. A*, 117, 14151-14162, 2013.  
 Vereecken, L., and Peeters, J., *Phys. Chem. Chem. Phys.*, 11, 9062-9074, 2009.  
 Wu, H., Wang, Y., Li, H., Huang, L., Huang, D., Shen, H., Xing, Y., and Chen, Z., *Atmos. Env.*, 164, 61-70, 2017.



Rate coefficients for the reaction  $\text{HO} + \text{CH}_3\text{C}(\text{O})\text{OOH}$ . The IUPAC recommendation follows the theoretical result of Berasategui et al. (2020).