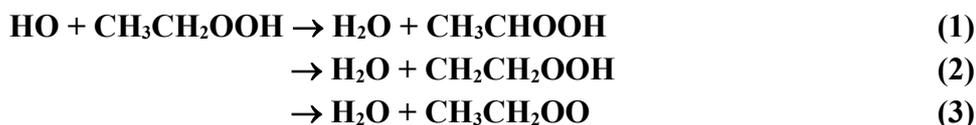


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOC65

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

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### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$(5.97 \pm 0.17) \times 10^{-12}$	$293 \pm 2$	Wang and Chen, 2008	RR (a,b)
$(6.10 \pm 0.31) \times 10^{-12}$	$293 \pm 2$	Wang and Chen, 2008	RR (a,c)
$(6.01 \pm 0.52) \times 10^{-12}$	$293 \pm 2$	Wang and Chen, 2008	RR (a,d)

### Comments

- (a) HO radicals were generated by the photolysis of O<sub>3</sub> at 254 nm in the presence of water vapor in 760 Torr (1.013 bar) total pressure of synthetic air. Experiments were carried out in a 28.5 L quartz reaction chamber. The concentrations of C<sub>2</sub>H<sub>5</sub>OOH and the reference compounds (cyclohexane, *m*-xylene and 1,3,5-trimethylbenzene) were measured by FTIR absorption spectroscopy. The reported rate coefficient ratios of  $k(\text{HO} + \text{C}_2\text{H}_5\text{OOH})/k(\text{HO} + \text{cyclohexane}) = 0.859 \pm 0.024$ ,  $k(\text{HO} + \text{C}_2\text{H}_5\text{OOH})/k(\text{HO} + \textit{m}\text{-xylene}) = 0.264 \pm 0.013$  and  $k(\text{HO} + \text{C}_2\text{H}_5\text{OOH})/k(\text{HO} + 1,3,5\text{-trimethylbenzene}) = 0.106 \pm 0.009$  are placed on an absolute basis by use of rate coefficients at 297 K of  $k(\text{HO} + \text{cyclohexane}) = 6.95 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k(\text{HO} + \textit{m}\text{-xylene}) = 2.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{HO} + 1,3,5\text{-trimethylbenzene}) = 5.67 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Arey, 2003). The synthesized sample of C<sub>2</sub>H<sub>5</sub>OOH was stated to be  $\geq 97\%$  purity as analyzed by FTIR spectroscopy. Concurrent photolysis of C<sub>2</sub>H<sub>5</sub>OOH at 254 nm was corrected for by measuring the photolysis rate of C<sub>2</sub>H<sub>5</sub>OOH in N<sub>2</sub>, with the correction for photolysis accounting for  $\sim 14\%$  of the C<sub>2</sub>H<sub>5</sub>OOH loss due to HO radical reaction (Wang and Chen, 2008).
- (b) Relative to cyclohexane.
- (c) Relative to *m*-xylene.
- (d) Relative to 1,3,5-trimethylbenzene.

### Preferred Values

$k > 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

*Comments on Preferred Values*

The only study of this reaction reported to date is that of Wang and Chen (2008). The rate coefficients obtained using three reference compounds are in excellent agreement. As noted in comment (a), C<sub>2</sub>H<sub>5</sub>OOH also underwent photolysis and a correction was made for this in deriving the reported rate coefficient ratios. Photolysis of C<sub>2</sub>H<sub>5</sub>OOH is expected to form HO radicals, C<sub>2</sub>H<sub>5</sub>OOH + hv → C<sub>2</sub>H<sub>5</sub>O + HO, and in the photolysis experiments carried out by Wang and Chen (2008) [see comment (a) above] these HO radicals would react with C<sub>2</sub>H<sub>5</sub>OOH, leading to some regeneration of HO radicals from decomposition of CH<sub>3</sub>CHOOH radicals formed after H-atom abstraction from the CH<sub>2</sub> group. In any case, it is likely that the photolysis rate of C<sub>2</sub>H<sub>5</sub>OOH was overestimated by Wang and Chen (2008) by a factor of at least 2, and the reported rate coefficient ratios are then lower limits. Furthermore, Wang and Chen (2008) conducted their experiments in air in the absence of NO, and under their conditions the HO radical-initiated reactions of C<sub>2</sub>H<sub>5</sub>OOH and the reference compounds are expected to produce HO<sub>2</sub> radicals. C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> radicals formed in channel (3) would have reacted with HO<sub>2</sub> radicals to reform C<sub>2</sub>H<sub>5</sub>OOH (Spittler et al., 2000; IUPAC, 2009). It is, however, not possible to assess the extent of re-formation of C<sub>2</sub>H<sub>5</sub>OOH after the occurrence of channel (3), and hence the underestimation of *k*, in the study of Wang and Chen (2008).

An average of the rate coefficients listed in the table is used as the basis for the lower limit to *k*. Clearly, further studies of this reaction are required.

### References

- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.  
IUPAC: <http://iupac.pole-ether.fr>, 2013.  
Spittler, M., Barnes, I., Becker, K. H. and Wallington, T. J.: Chem. Phys. Lett., 321, 57, 2000.  
Wang, C. and Chen, Z.: Atmos. Environ., 42, 6614, 2008.