

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOC34

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This data sheet last evaluated: 18<sup>th</sup> December 2007 (with revision of the preferred values).



$$\Delta H^\circ(2) = -139 \text{ kJ}\cdot\text{mol}^{-1}$$

### 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>			
$2.93 \times 10^{-12} \exp[(190 \pm 14)/T]$	223-423	Vaghjiani and Ravishankara, 1989	PLP-LIF (a)
$5.54 \times 10^{-12}$	298		
$k_2 = 1.78 \times 10^{-12} \exp[(220 \pm 21)/T]$	203-348	Vaghjiani and Ravishankara, 1989	PLP-LIF (a)
$k_2 = (3.85 \pm 0.23) \times 10^{-12}$	298		
$k_2 = (9.0 \pm 0.2) \times 10^{-12}$	295	Blitz et al., 2005	PLP-LIF (b)
<i>Relative Rate Coefficients</i>			
$(1.02 \pm 0.08) \times 10^{-11}$	~298	Niki et al., 1983	RR (c)
$(1.02 \pm 0.11) \times 10^{-11}$	~298	Niki et al., 1983	RR (d)
<i>Branching Ratio</i>			
$k_1/k_2 = 0.77 \pm 0.16$	~298	Niki et al., 1983	(e)

### Comments

- (a) H<sup>16</sup>O, H<sup>18</sup>O and DO radicals were generated by flash photolysis or pulsed laser photolysis of the following precursors: for H<sup>16</sup>O; CH<sub>3</sub>OOH, H<sub>2</sub><sup>16</sup>O, and O<sub>3</sub>-H<sub>2</sub><sup>16</sup>O; for H<sup>18</sup>O; H<sub>2</sub><sup>18</sup>O, and O<sub>3</sub>-H<sub>2</sub><sup>18</sup>O; and for DO; D<sub>2</sub>O, O<sub>3</sub>-D<sub>2</sub>O, and O<sub>3</sub>-D<sub>2</sub>, and H<sup>16</sup>O, H<sup>18</sup>O and DO radicals were monitored by LIF. Rate coefficients ( $k_1 + k_2$ ) were obtained from measurements of the decay rates of H<sup>18</sup>O and DO radicals in the presence of excess CH<sub>3</sub>OOH. Rate coefficients  $k_2$  were obtained from the decay rates of H<sup>16</sup>O radicals in the presence of CH<sub>3</sub>OOH. The CH<sub>2</sub>OOH radical formed in reaction channel (1) rapidly decomposes to HO + HCHO, and hence the use of H<sup>16</sup>O allowed only the rate coefficient  $k_2$  to be measured. The purity of the CH<sub>3</sub>OOH in the synthesized sample was stated to be >96%, and the concentration of CH<sub>3</sub>OOH in the flowing gas stream was monitored by UV absorption at 213.9 nm either prior to, or in some cases after, entering the reaction cell.
- (b) HO radicals were generated by pulsed laser photolysis of CH<sub>3</sub>OOH at 248 nm, and were monitored by LIF. Since the CH<sub>2</sub>OOH radical formed in reaction channel (1) rapidly decomposes to HO + HCHO (Vaghjiani and Ravishankara, 1989) the use of H<sup>16</sup>O allowed only the rate coefficient  $k_2$  to be measured. The purity of the CH<sub>3</sub>OOH in the synthesized sample was determined using reverse phase HPLC, and was shown to be <99.5%. The concentration of CH<sub>3</sub>OOH was not measured in the reactant gas stream.
- (c) HO radicals were generated by the photolysis of CH<sub>3</sub>ONO or C<sub>2</sub>H<sub>5</sub>ONO in air. The concentrations of CH<sub>3</sub>OOH and ethene (the reference compound) were measured by FTIR absorption

spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_3\text{OOH})/k(\text{HO} + \text{ethene}) = 1.20 \pm 0.09$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and atmospheric pressure of air (Atkinson, 1997).

- (d) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  in air and the concentrations of  $\text{CH}_3\text{OOH}$  and  $\text{CH}_3\text{CHO}$  (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_3\text{OOH})/k(\text{HO} + \text{CH}_3\text{CHO}) = 0.68 \pm 0.07$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{CH}_3\text{CHO}) = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).
- (e) Derived from the yield ratio of  $(\text{HCHO} + \text{CO})/(\text{CH}_3\text{ONO} + \text{CH}_3\text{ONO}_2)$  in experiments carried out using ethyl nitrite as the HO radical precursor and at  $\text{O}_2$  partial pressures of 20-140 Torr, extrapolated to zero  $[\text{O}_2]$ . Channel (1) leads to HCHO, with CO being formed from the secondary reaction  $\text{HO} + \text{HCHO}$ , while channel (2) leads to  $\text{CH}_3\text{O}$  radicals which at low  $\text{O}_2$  concentrations react with NO and  $\text{NO}_2$  to form methyl nitrite and methyl nitrate. At higher  $\text{O}_2$  concentrations, the  $\text{CH}_3\text{O} + \text{O}_2$  reaction leads to HCHO formation, hence the extrapolation to zero  $[\text{O}_2]$ . The measured branching ratio corresponds to  $k_1/k = 0.435 \pm 0.10$ .

### Preferred Values

$k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 5.3 \times 10^{-12} \exp(190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220-430 K.

$k_1/k = 0.4$ , independent of temperature over the range 220-430 K.

#### Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

$\Delta(E/R) = \pm 200$  K.

$\Delta(k_1/k) = \pm 0.15$  over the temperature range 220-430 K.

#### Comments on Preferred Values

There are significant discrepancies between the results of the studies of Niki et al. (1983), Vaghjiani and Ravishankara (1989) and Blitz et al. (2005). The room temperature values of  $k_2$  measured directly (Vaghjiani and Ravishankara, 1989; Blitz et al., 2005) or derived from the branching ratio and overall rate coefficient (Niki et al., 1983) are  $(3.85 \pm 0.23) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Vaghjiani and Ravishankara, 1989),  $(5.8 \pm 1.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Niki et al., 1983) and  $(9.0 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Blitz et al., 2005). The two room temperature measurements of  $k$  disagree by a factor of 1.85 (Niki et al., 1983; Vaghjiani and Ravishankara, 1989), while the branching ratio  $k_2/k = 0.70$  obtained from the separate measurements of  $k_2$  and  $k$  by Vaghjiani and Ravishankara (1989) is in reasonable agreement with that of Niki et al. (1983) of  $0.565 \pm 0.10$ .

The reasons for these discrepancies concerning the room temperature rate coefficients  $k_2$  and  $k$  are not presently known. Since the relative rate method used by Niki et al. (1983) does not require a knowledge of the absolute concentration of  $\text{CH}_3\text{OOH}$  (but does require that  $\text{CH}_3\text{OOH}$  can be monitored free of interferences from other species), then the rate coefficient  $k$  measured by Niki et al. (1983) is used for the preferred 298 K value. Although confirmatory studies are clearly required, the temperature dependence obtained by Vaghjiani and Ravishankara (1989) is accepted, with large uncertainties, and the pre-exponential factor is adjusted to fit the preferred 298 K value. The preferred branching ratio is derived from the data of Niki et al. (1983) and Vaghjiani and Ravishankara (1989), again with a large uncertainty. Clearly, further studies of this reaction are needed.

### References

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