

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOC13

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This data sheet last evaluated: 16<sup>th</sup> October 2007; revision of preferred values.

## HO + C<sub>2</sub>H<sub>5</sub>CHO → products

### Rate coefficient data

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
(1.71 ± 0.24) × 10 <sup>-11</sup>	298	Semmes et al., 1985	FP-RF
5.3 × 10 <sup>-11</sup> exp[(405 ± 30)/T]	240-372	Thévenet et al., 2000	PLP-LIF
(2.0 ± 0.3) × 10 <sup>-11</sup>	298		
<i>Relative Rate Coefficients</i>			
(2.22 ± 0.09) × 10 <sup>-11</sup>	298 ± 2	Niki et al., 1978	RR (a)
(1.94 ± 0.15) × 10 <sup>-11</sup>	298 ± 4	Kerr and Sheppard, 1981	RR (b)
(2.00 ± 0.14) × 10 <sup>-11</sup>	296 ± 2	Papagni et al., 2000	RR (c)
(1.89 ± 0.16) × 10 <sup>-11</sup>	298 ± 2	D'Anna et al., 2001	RR (d)
(1.85 ± 0.15) × 10 <sup>-11</sup>	295 ± 1	Le Crâne et al., 2005	RR (e,f)
(1.65 ± 0.10) × 10 <sup>-11</sup>	295 ± 1	Le Crâne et al., 2005	RR (e,g)

### Comments

- HO radicals were generated by the photolysis of HONO in air and the concentrations of propanal and ethene (the reference compound) were measured by FTIR absorption spectroscopy during the experiments. The measured rate coefficient ratio of  $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{ethene}) = 2.6 \pm 0.1$  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 (Atkinson, 1997).
- HO radicals were generated by the photolysis of HONO in air, and the concentrations of propanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of  $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{ethene}) = 2.28 \pm 0.17$  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 (Atkinson, 1997).
- HO radicals were generated by the photolysis of CH<sub>3</sub>ONO in air and the concentrations of propanal and methyl vinyl ketone (the reference compound) were measured by GC. The measured rate coefficient ratio of  $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{methyl vinyl ketone}) = 0.982 \pm 0.065$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{methyl vinyl ketone}) = 2.04 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K (IUPAC, 2007).
- HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of propanal and propene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{propene}) = 0.72 \pm 0.06$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and atmospheric pressure of air (Atkinson 1997).

- (e) HO radicals were generated by the photolysis of CH<sub>3</sub>ONO in air at 700 Torr (933 mbar) pressure and the concentrations of propanal and ethene or propene (the reference compounds) were measured by FTIR spectroscopy. The measured rate coefficient ratios of  $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{ethene}) = 2.14 \pm 0.17$  and  $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{propene}) = 0.614 \pm 0.037$  are placed on an absolute basis by use of a rate coefficients at 295 K and atmospheric pressure of air of  $k(\text{HO} + \text{ethene}) = 8.65 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{HO} + \text{propene}) = 2.68 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 1997).
- (f) Relative to ethene.
- (g) Relative to propene.

### Preferred Values

$k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 4.9 \times 10^{-12} \exp(405/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240-380 K

### Reliability

$\Delta \log k = \pm 0.10$  at 298 K.

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

### Comments on Preferred Values

The preferred 298 K rate coefficient is derived from the mean of the room temperature absolute rate coefficient of Semmes et al. (1985) and Thévenet et al. (2000) and the relative rate coefficients of Niki et al. (1978), Kerr and Sheppard (1981), Papagni et al. (2000), D'Anna et al. (2001) and Le Crâne et al. (2005). The temperature dependence is that measured by Thévenet et al. (2000) and the pre-exponential factor is adjusted to fit the 298 K preferred value. The relative rate coefficient of Audley et al. (1981) was not used in the evaluation, due to questions concerning the applicability of the experimental technique used (Semmes et al., 1985; Atkinson, 1989).

At 290 K, Vandenberg and Peeters (2003) measured a H<sub>2</sub>O yield from this reaction of  $100 \pm 10\%$ , with formation of HC(O)OH (which could be formed via an addition-elimination reaction) accounting for <3% off the overall reaction. These data of Vandenberg and Peeters (2003) show that the reaction proceeds by H-atom abstraction at room temperature. The major reaction channel is expected to be H-atom abstraction from the -CHO group to form H<sub>2</sub>O + C<sub>2</sub>H<sub>5</sub>CO.

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