

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx\_VOC17

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This data sheet updated: 18<sup>th</sup> October 2007 (with revisions to the preferred values).



## 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>			
$(8.0 \pm 0.8) \times 10^{-12}$	240-362	Karunananand et al., 2007	PLP-LIF (a)
<i>Relative Rate Coefficients</i>			
$(9.40 \pm 0.90) \times 10^{-12}$	$298 \pm 2$	Niki et al., 1987	RR (b)
$(1.24 \pm 0.16) \times 10^{-11}$	298	Bacher et al., 2001	RR (b,c)
$(1.03 \pm 0.07) \times 10^{-11}$	298	Bacher et al., 2001	RR (c,d)
$(1.22 \pm 0.20) \times 10^{-11}$	$296 \pm 2$	Baker et al., 2004	RR (e,f)
$(7.9 \pm 1.6) \times 10^{-12}$	$296 \pm 2$	Baker et al., 2004	RR (e,g)
$(1.08 \pm 0.08) \times 10^{-11}$	$298 \pm 3$	Magneron et al., 2005	RR (h,i)
$(1.33 \pm 0.15) \times 10^{-11}$	$298 \pm 3$	Magneron et al., 2005	RR (h,j)
$(1.09 \pm 0.09) \times 10^{-11}$	$298 \pm 3$	Magneron et al., 2005	RR (h,k)
$(1.38 \pm 0.17) \times 10^{-11}$	$298 \pm 3$	Magneron et al., 2005	RR (h,l)
<i>Branching Ratios</i>			
$k_1/k = 0.80$	$298 \pm 2$	Niki et al., 1987	(m)
$k_2/k = 0.20$	$298 \pm 2$	Niki et al., 1987	(m)
$k_2/k = 0.22 \pm 0.06$	$\sim 298$	Magneron et al., 2005	(n)

## Comments

- (a) HO and DO radicals were generated by the photolysis of H<sub>2</sub>O<sub>2</sub> and D<sub>2</sub>O<sub>2</sub>, respectively, at 248 nm, by the 248 nm photolysis of O<sub>3</sub> in the presence of CH<sub>4</sub>, and by the photolysis of HOCH<sub>2</sub>CHO at 248 nm. Generation of HO radicals from the photolysis of O<sub>3</sub>-CH<sub>4</sub> mixtures generally resulted in bi-exponential HO radical decays, attributed to HO radical regeneration from formation of H atoms from the reaction of O(<sup>1</sup>D) atoms with CH<sub>4</sub> and their subsequent reaction with O<sub>3</sub>. Total pressure was varied from 60 Torr (80 mbar) of He diluent to 250 Torr (333 mbar) of N<sub>2</sub>, with the measured rate coefficients being independent of pressure over this range, and of the HO radical generation method. The rate coefficients at 278 K, 297 K and 337 K for the DO + HOCH<sub>2</sub>CHO reaction were ~10% higher than the corresponding HO radical reaction rate coefficients.
- (b) HO radicals were generated by the photolysis of CH<sub>3</sub>ONO in air and the concentrations of HOCH<sub>2</sub>CHO and acetaldehyde (the reference compound) measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{HOCH}_2\text{CHO}) = 1.6 \pm 0.15$  (Niki et al., 1987) and  $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + \text{CH}_3\text{CHO}) = 1.03 \pm 0.13$  (Bacher et al., 2001) are 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).

- (c) Wall losses were estimated (Bacher et al., 2001) to have led to a ~20% overestimation of the HO radical reaction rate coefficients. The rate coefficients cited in the table are the rate coefficients calculated from the measured rate coefficient ratios, reduced by 20%.
- (d) HO radicals were generated by the photolysis of CH<sub>3</sub>ONO in air and the concentrations of HOCH<sub>2</sub>CHO and propene (the reference compound) measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + \text{propene}) = 0.49 \pm 0.03$  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. HOCH<sub>2</sub>CHO was generated in situ from the OH radical-initiated reaction of 1,2-butanediol or 2-methyl-3-buten-2-ol, and the concentrations of HOCH<sub>2</sub>CHO and its precursor measured by GC. From comparison of the measured time-concentration behaviour of HOCH<sub>2</sub>CHO and its precursor with calculations, rate coefficient ratios of  $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + 1,2\text{-butanediol}) = 0.485 \pm 0.073$  and  $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + 2\text{-methyl-3-buten-2-ol}) = 0.124 \pm 0.025$  were derived. These rate coefficient ratios are placed on an absolute basis by use of rate coefficients at 296 K of  $k(\text{HO} + 1,2\text{-butanediol}) = (2.51 \pm 0.13) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Baker et al., 2004) and  $k(\text{HO} + 2\text{-methyl-3-buten-2-ol}) = 6.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (f) Relative to 1,2-butanediol.
- (g) Relative to 2-methyl-3-buten-2-ol.
- (h) HO radicals were generated by the photolysis of HONO in air and the concentrations of HOCH<sub>2</sub>CHO and diisopropyl ether, diethyl ether, 1,3-dioxolane or acetaldehyde (the reference compounds) measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of  $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + \text{diisopropyl ether}) = 1.06 \pm 0.07$ ,  $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + \text{diethyl ether}) = 0.98 \pm 0.11$ ,  $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + 1,3\text{-dioxolane}) = 0.98 \pm 0.08$  and  $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + \text{acetaldehyde}) = 0.92 \pm 0.11$  are placed on an absolute basis by use of rate coefficients at 298 K of  $k(\text{HO} + \text{diisopropyl ether}) = 1.02 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Magneron et al., 2005),  $k(\text{HO} + \text{diethyl ether}) = 1.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Magneron et al., 2005),  $k(\text{HO} + 1,3\text{-dioxolane}) = 1.11 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Magneron et al., 2005) and  $k(\text{HO} + \text{acetaldehyde}) = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (i) Relative to diisopropyl ether.
- (j) Relative to diethyl ether.
- (k) Relative to 1,3-dioxolane.
- (l) Relative to acetaldehyde.
- (m) HO radicals were generated by the photolysis of ethyl nitrite in air, and HOCH<sub>2</sub>CHO and the products (CHO)<sub>2</sub>, CO<sub>2</sub> and HCHO were measured by FTIR absorption spectroscopy. Product formation yields of (CHO)<sub>2</sub>,  $21.1 \pm 2.4\%$ ; CO<sub>2</sub>,  $81.3 \pm 3.2\%$ ; and HCHO,  $82.4 \pm 4.6\%$  were obtained, leading to branching ratios of  $k_1/k = 0.80$  and  $k_2/k = 0.20$ .
- (n) HO radicals were generated by photolysis of HONO in air in the EUPHORE chamber, and HOCH<sub>2</sub>CHO and the products HCHO, CO and (CHO)<sub>2</sub> were monitored by FTIR spectroscopy. The measured glyoxal yield of  $22 \pm 6\%$  was attributed to channel (2). The initial HCHO yield was  $64 \pm 5\%$ .

### Preferred Values

$k = 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 240–370 K.  
 $k_1/k = 0.80$  at 298 K.  
 $k_2/k = 0.20$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.15$  at 298 K.  
 $\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.10$  at 298 K.

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

#### *Comments on Preferred Values*

The rate coefficients from relative rate studies conducted at room temperature show an appreciable amount of scatter, ranging from  $7.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to  $1.38 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The sole absolute rate study of Karunanandan et al. (2007) is at the lower end of this range, with a temperature independent rate coefficient over the range 240-362 K. This temperature-independent rate coefficient of Karunanandan et al. (2007) is accepted as the preferred value. The branching ratios  $k_1/k$  and  $k_2/k$  are taken from the studies of Niki et al. (1987) and Magneron et al. (2005), which are in good agreement. The product study of Butkovskaya et al. (2002), carried out at 200 Torr (267 mbar) pressure, is consistent with the preferred branching ratio, with derived values of  $k_1/k = 0.84$  and  $k_2/k = 0.16$  at 296 K and 200 Torr total pressure.

#### References

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