

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOC55

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### HO<sub>2</sub> + HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> → products

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(4.8 \pm 1.5) \times 10^{-12}$	298	Jenkin and Cox, 1991	MM-UVA (a)
$\approx 2.0 \times 10^{-11}$	298	Anastasi et al., 1991	PR-UVA (b)
$(1.2 \pm 0.3) \times 10^{-11}$	296	Murrells et al., 1991	PLP-UVA (c)
$(1.5 \pm 0.3) \times 10^{-11}$	296	Jenkin and Hayman, 1995	PLP-UVA (d)
$(1.17 \pm 0.22) \times 10^{-11}$	298	Boyd et al., 2003	PLP-UVA (e)

#### Comments

- MM study with HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> radicals being generated from the photolysis of HOCH<sub>2</sub>CH<sub>2</sub>I in the presence of O<sub>2</sub> and N<sub>2</sub> at total pressures of 13 mbar, 133 mbar and 1013 mbar (10 Torr, 100 Torr, and 760 Torr) in a slow flow system. The modulated absorption spectrum in the range 205 nm to 310 nm showed that additional transient species were absorbing, and these were ascribed to HOCH<sub>2</sub>CH<sub>2</sub>OOI and HO<sub>2</sub>. The rate coefficient was obtained from computer simulations of the time-resolved absorption waveforms at 220 nm to 310 nm for experiments at 13 mbar (10 Torr) pressure.
- Pulse-radiolysis study, with HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> radicals being generated from CH<sub>4</sub>-O<sub>2</sub>-H<sub>2</sub>O-SF<sub>6</sub> and CH<sub>3</sub>CH<sub>2</sub>OH-O<sub>2</sub>-SF<sub>6</sub> mixtures at total pressures of 1013 mbar (760 Torr). [HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>] was monitored by absorption at 230 nm and  $k$  derived from kinetic modelling of absorption profiles.
- Pulsed laser photolysis study, with HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> radicals being generated from photolysis of HOCH<sub>2</sub>CH<sub>2</sub>Cl in the presence of O<sub>2</sub> and N<sub>2</sub> at total pressures of 973 mbar (730 Torr). The rate coefficient was obtained by modelling the observed absorption profiles on the basis of a simplified mechanism of four reactions.
- PLP-UV absorption study of H<sub>2</sub>O<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures at 1 bar (750 Torr) and 296 K. Conditions were chosen such that the initial concentration ratios, [HO<sub>2</sub>]/[HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>], were varied in the range 1.1 – 5.3.  $k$  was determined from simulation of transient decay traces recorded at 220 nm, 230 nm and 260 nm, with different relative contributions to the signals being due to HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub> absorption.
- PLP-UV absorption study of H<sub>2</sub>O<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures at 1013 mbar (760 Torr) and 298 K. Conditions were chosen such that HO<sub>2</sub> was in excess, with initial concentration ratios [HO<sub>2</sub>]/[HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>] in the range 4 - 10.  $k$  was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> absorption, with its decay being almost entirely due to the reaction with HO<sub>2</sub>. The signal at 210 nm or 220 nm was mainly due to HO<sub>2</sub> absorption, with its self-reaction making the major contribution to its removal.

### Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.3 \times 10^{-11}$	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.2$	298

#### Comments on Preferred Values

The preferred value of  $k$  is based on the results of the pulsed laser photolysis studies of Murrells et al. (1991), Jenkin and Hayman (1995) and Boyd et al. (2003), which are in good agreement.

The earlier determinations of Jenkin and Cox (1991) and Anastasi et al. (1991) were subject to errors in the magnitude and shape of the  $\text{HOCH}_2\text{CH}_2\text{O}_2$  absorption spectrum, respectively, which influenced the derived values of  $k$ . Murrells et al. (2001) demonstrated that cross-sections reported by Jenkin and Cox (1991), from molecular modulation studies of the photolysis of  $\text{HOCH}_2\text{CH}_2\text{I}$ , are low by a factor of approximately two. Jenkin and Cox (1991) made the assumption that the photolysis of  $\text{HOCH}_2\text{CH}_2\text{I}$  in their system yielded entirely  $\text{HOCH}_2\text{CH}_2\text{O}_2$  radicals, which was apparently not the case. Increasing  $\sigma_{230}(\text{HOCH}_2\text{CH}_2\text{O}_2)$  by a factor of two in a re-interpretation (Murrells et al., 1991) of the data of Jenkin and Cox (1991) yielded a revised value of  $k = (8.4 \pm 3.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 13 mbar pressure, in fair agreement with the current recommendation (which is based on measurements at close to 1 bar). The approximate value of  $k$  of Anastasi et al. (1991), derived from pulsed radiolysis experiments, is also within the uncertainty range on our preferred value. However, we have not taken this value of Anastasi et al. (1991) into account, because of the differences in the absorption spectrum of the radical observed, compared with the consistent spectra shapes reported by Jenkin and Cox (1991) and Murrells et al. (1991) (see the data sheet for the reaction  $2 \text{HOCH}_2\text{CH}_2\text{O}_2 \rightarrow \text{products}$ ).

Barnes et al. (1993) observed evidence for the formation of  $\text{HOCH}_2\text{CH}_2\text{OOH}$  in their product study of the self reaction of  $\text{HOCH}_2\text{CH}_2\text{O}_2$ . The estimated yield was consistent with its formation from the secondary reaction of  $\text{HO}_2$  with  $\text{HOCH}_2\text{CH}_2\text{O}_2$ , and suggested that the reaction mainly yields  $\text{HOCH}_2\text{CH}_2\text{OOH}$  and  $\text{O}_2$ , although further studies are required to confirm this. Dillon and Crowley (2008) have investigated the formation of HO from the reactions of  $\text{HO}_2$  with selected  $\text{RO}_2$  radicals. In the case of  $\text{HOCH}_2\text{CH}_2\text{O}_2$ , an upper limit of 0.04 was reported for the product channel forming HO,  $\text{HOCH}_2\text{CH}_2\text{O}$  and  $\text{O}_2$ .

### References

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