

## Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox\_VOC9

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### O<sub>3</sub> + CH<sub>2</sub>=C(CH<sub>3</sub>)CHO (methacrolein) → 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>			
(1.12 ± 0.13) × 10 <sup>-18</sup>	296 ± 2	Atkinson et al., 1981	S-CL
1.1 × 10 <sup>-18</sup>	~ 294	Kamens et al., 1982	S-CL/GC (a)
1.3 × 10 <sup>-15</sup> exp[-(2112 ± 131)/T]	240-324	Treacy et al., 1992	S-UVA
(1.1 ± 0.2) × 10 <sup>-18</sup>	298		
(1.02 ± 0.05) × 10 <sup>-18</sup>	291 ± 2	Grosjean et al., 1993	S-UVA
(1.08 ± 0.20) × 10 <sup>-18</sup>	290 ± 1	Grosjean and Grosjean, 1998	S-UVA
(1.3 ± 0.14) × 10 <sup>-18</sup>	296 ± 2	Neeb et al., 1998	S-FTIR (b)

#### Comments

- (a) Carried out at atmospheric pressure of air in a large outdoor chamber at night. O<sub>3</sub> was introduced continually over a period of ~ 5 hrs to a methacrolein-air mixture. The methacrolein and O<sub>3</sub> concentrations were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured methacrolein and O<sub>3</sub> concentrations to a computer model.
- (b) The decays of methacrolein were measured in the presence of excess concentrations of O<sub>3</sub>, with cyclohexane also being present as an HO radical scavenger.

#### Preferred Values

$k = 1.2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.4 \times 10^{-15} \exp(-2100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240-330 K.

#### Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \pm 300$  K.

#### Comments on Preferred Values

The measured room temperature rate coefficients of Atkinson et al. (1981), Kamens et al. (1982), Treacy et al. (1992), Grosjean et al. (1993), Grosjean and Grosjean (1998) and Neeb et al. (1998) are in good agreement. The preferred 298 K rate coefficient is the average of the measured rate

coefficients from these studies (Atkinson et al., 1981; Kamens et al., 1982; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998), adjusted to 298 K where necessary using the temperature dependence of Treacy et al. (1992). The temperature dependence measured by Treacy et al. (1992) is accepted, and is combined with the 298 K preferred value to obtain the pre-exponential factor.

The reaction proceeds by initial addition of O<sub>3</sub> to the C=C bond to form a primary ozonide which rapidly decomposes to methylglyoxal + [CH<sub>2</sub>OO]\* or to formaldehyde + [CH<sub>3</sub>C(OO)CHO]\* (see IUPAC (2007) data sheets on the reactions of O<sub>3</sub> with ethene and propene). Methylglyoxal and formaldehyde have been observed as significant products of this reaction, with formation yields of 52-64% and 9-15%, respectively (Grosjean et al., 1993), indicating that formation of methylglyoxal + [CH<sub>2</sub>OO]\* dominates. HO radicals are also formed, with a reported yield of 20<sup>+10</sup><sub>-13</sub> % (Aschmann et al., 1996).

### References

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