

Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC10

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O₃ + CH₃C(O)CH=CH₂ (methyl vinyl ketone) → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
(4.77 ± 0.59) × 10 ⁻¹⁸	296 ± 2	Atkinson et al., 1981	S-CL
4.0 × 10 ⁻¹⁸	~ 294	Kamens et al., 1982	S-CL/GC (a)
6.9 × 10 ⁻¹⁶ exp[-(1521 ± 78)/T]	240-324	Treacy et al., 1992	S-UVA
(4.2 ± 0.4) × 10 ⁻¹⁸	298		
(4.72 ± 0.09) × 10 ⁻¹⁸	291 ± 2	Grosjean et al., 1993	S-UVA
(5.84 ± 0.39) × 10 ⁻¹⁸	291 ± 1	Grosjean and Grosjean, 1998	S-UVA
(5.4 ± 0.6) × 10 ⁻¹⁸	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. O₃ was introduced continually over a period of ~ 5 hrs to a methyl vinyl ketone-air mixture. The methyl vinyl ketone and O₃ concentrations were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured methyl vinyl ketone and O₃ concentrations to a computer model.
- (b) The decays of methyl vinyl ketone were measured in the presence of excess concentrations of O₃, with cyclohexane also being present as an HO radical scavenger.

Preferred Values

$k = 5.2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 8.5 \times 10^{-16} \exp(-1520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240-330 K.

Reliability

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

$\Delta(E/R) = \pm 200$ 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) range over a factor of 1.5, with the temperature dependent study of Treacy et al. (1992) having the lowest measured rate coefficient (taking into account the actual value of room temperature in the various studies). The preferred 298 K rate coefficient is the average of the measured room temperature rate

coefficients (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 O₃ to the C=C bond to form a primary ozonide which rapidly decomposes to methylglyoxal + [CH₂OO]* or to formaldehyde + [CH₃C(O)CHOO]* (see data sheets (IUPAC, 2007) on the reactions of O₃ with ethene and propene). Methylglyoxal has been observed as a major product of this reaction, with a formation yield of 82-92% (Grosjean et al., 1993), indicating that formation of methylglyoxal + [CH₂OO]* dominates. HO radicals are also formed, with measured yields of 16 ± 8% (Aschmann et al., 1996) and 16 ± 5% (Paulson et al., 1998).

References

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