IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC9

O_3 + CH_2=$C(CH_3)CHO$ (methacrolein) $\rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(1.12 ± 0.13) x 10^{-18}	296 ± 2	Atkinson et al., 1981	S-CL
1.1 x 10^{-18}	~294	Kamens et al., 1982	S-CL/GC (a)
1.3 x 10^{-15} exp[-$(2112 \pm 131)/T$]	240-324	Treacy et al., 1992	S-UVA
(1.1 ± 0.2) x 10^{-18}	298		
(1.02 ± 0.05) x 10^{-18}	291 ± 2	Grosjean et al., 1993	S-UVA
(1.08 ± 0.20) x 10^{-18}	290 ± 1	Grosjean and Grosjean, 1998	S-UVA
(1.3 ± 0.14) x 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. O_3 was introduced continually over a period of ~5 hrs to a methacrolein-air mixture. The methacrolein and O_3 concentrations were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured methacrolein and O_3 concentrations to a computer model.

(b) The decays of methacrolein were measured in the presence of excess concentrations of O_3, with cyclohexane also being present as an HO radical scavenger.

Preferred Values

k = 1.2 x 10^{-18} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 1.4 x 10^{-15} exp(-2100/T) cm^3 molecule^{-1} 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_3 to the C=C bond to form a primary ozonide which rapidly decomposes to methylglyoxal + $[CH_2OO]^*$ or to formaldehyde + $[CH_3C(OO)CHO]^*$ (see IUPAC (2007) data sheets on the reactions of O_3 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 + $[CH_2OO]^*$ dominates. HO radicals are also formed, with a reported yield of 20^{+10}_{-13} % (Aschmann et al., 1996).

References

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