IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet R_Oxygen_2

This data sheet updated: 22nd November 2006.

$CH_3 + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$5.1 \times 10^{-12} \exp[-(210 \pm 84)/T]$	243-384	Ogryzlo et al., 1981	FP-MS (a)
$(2.53 \pm 0.54) \times 10^{-12}$	298	Paltenghi et al., 1984	
$(2.2 \pm 0.2) \times 10^{-12}$	298	Albaladejo et al., 2002	PLP-LIF (b)

Comments

(a) Flash photolysis of CH_3NO_2 at 193 nm in a flow system with He carrier gas at pressures of ~2.7 mbar (~2 Torr). [CH_3] was monitored by photoionization MS under pseudo-first-order conditions; no product analyses. The original data (Ogryzlo et al., 1981) were revised (Paltenghi et al., 1984) on the basis of a correction for the pressure drop along the flow tube between the reaction vessel and the manometer.

(b) Pulsed laser photolysis of CH_3Br at 193 nm and 133 mbar (100 Torr) He coupled with laser-excited fluorescence detection of CH_3O at 292.4 nm in a slow-flow cell. The rate coefficient for total removal of CH_3 was determined by numerical analysis of the temporal profiles of the CH_3O signal. The calibration of the CH_3O concentration was performed by comparing LIF signals with those for the reaction $CH_3 + NO_2$ obtained under identical conditions. The CH_3O absolute yield is 0.044 ± 0.013 and leads to $k = (9.68 \pm 1.10) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for the reaction $CH_3 + NO_2 \rightarrow CH_3O + O_2$.

Preferred Values

$k = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.7 \times 10^{-12} \exp(-210/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240 to 400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the mean of the revised calculations by Paltenghi et al. (1984) of the earlier data of Ogryzlo et al. (1981) and of the data of Albaladejo et al. (2002).

References

Albaladejo, J., Jimenez, E., Notario, A., Cabañas, B., and Martinez, E.: J. Phys. Chem. A 106, 2512, 2002.
Ogryzlo, E. A., Paltenghi, R., and Bayes, K. D.: Int. J. Chem. Kinet. 13, 667, 1981.
Paltenghi, R., Ogryzlo, E. A., and Bayes, K. D.: J. Phys. Chem. 88, 2595, 1984.