IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC16

This data sheet updated: 12th December 2007 (with no revision of the preferred values).

NO_3 + CH_2=C(CH_3)CHO (methacrolein) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$\leq 8 \times 10^{-15}$	298	Rudich et al., 1996	F-A (a)
Relative Rate Coefficients			
$(4.46 \pm 0.58) \times 10^{-15}$	296 ± 2	Kwok et al., 1996	RR (b)
$(3.08 \pm 0.18) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (c)
$(3.50 \pm 0.15) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (d)
$(3.72 \pm 0.47) \times 10^{-15}$	296 ± 2	Canosa-Mas et al., 1999	RR (e)

Comments

(a) NO_3 radicals were generated by thermal decomposition of N_2O_5 in a flow system at total pressures of 1.5-3 Torr (2-4 mbar), and monitored by absorption at 661.9 nm.

(b) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3$ + methacrolein$)/k(NO_3$ + propene$) = 0.48 \pm 0.06$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + propene$) = 9.29 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

(c) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3$ + methacrolein$)/k(NO_3$ + propene$) = 0.324 \pm 0.017$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + propene$) = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(d) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methacrolein and 1-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3$ + methacrolein$)/k(NO_3$ + 1-butene$) = 0.259 \pm 0.011$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + 1-butene$) = 1.35 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 1997).

(e) Relative rate method carried out at atmospheric pressure of N_2. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3$ + methacrolein$)/k(NO_3$ + propene$) = 0.40 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + propene$) = 9.29 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current

recommendation). An absolute rate coefficient of (9.6 ± 2.0) x 10^{-15} cm^3 $molecule^{-1}$ s^{-1} was also measured at 300 ± 7 K using a discharge flow system with LIF detection of NO_3 radicals.

Preferred Values

k = 3.4 x 10^{-15} cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The 298 K preferred value is the average of the relative rate coefficients of Chew et al. (1998) (which supersedes the earlier and less extensive study of Kwok et al., 1996) and Canosa-Mas et al. (1999), which are in good agreement and are consistent with the upper limit reported by Rudich et al. (1996).

The room temperature rate coefficient is similar to that for reaction of NO_3 radicals with acetaldehyde (IUPAC, 2007), and the reaction is expected to proceed mainly by H-atom abstraction from the CHO group.

References

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