IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet NO3_VOC15
Website: http://www.iupac-kinetic.ch.cam.ac.uk/. See website for latest evaluated data. This datasheet updated: 21st October 2002.

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

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
≤8 x 10^{-15}	298	Rudich *et al*., 1996[1]	F-A (a)
Relative Rate Coefficients			
(4.46 ± 0.58) x 10^{-15}	296 ± 2	Kwok *et al*., 1996[2]	RR (b)
(3.08 ± 0.18) x 10^{-15}	298 ± 2	Chew, Atkinson, and Aschmann, 1997[3]	RR (c)
(3.50 ± 0.15) x 10^{-15}	298 ± 2	Chew, Atkinson, and Aschmann, 1997[3]	RR (d)
(3.72 ± 0.47) x 10^{-15}	296 ± 2	Canosa-Mas *et al*., 1999[4]	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 $k(NO_3 + \text{methacrolein})/k(NO_3 + \text{propene}) = 0.48 \pm 0.06$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.29 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K.[5]

(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 $k(NO_3 + \text{methacrolein})/k(NO_3 + \text{propene}) = 0.324 \pm 0.017$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.[5]

(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 $k(NO_3 + \text{methacrolein})/k(NO_3 + \text{1-butene}) = 0.259 \pm 0.011$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{1-butene}) = 1.35 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.[6]

(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.[5] An absolute rate coefficient of $(9.6 \pm 2.0) \times 10^{-15}$ 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

$k = 3.4 \times 10^{-15}$ 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*.[3] (which supersedes the earlier and less extensive study of Kwok *et al*.[2]) and Canosa-Mas *et al*.,[4] which are in good agreement and are consistent with the upper limit reported by Rudich *et al*.[1]

The room temperature rate coefficient is similar to that for reaction of NO_3 radicals with acetaldehyde,[5] and the reaction is expected to proceed mainly by H-atom abstraction from the CHO group

References

1 Y. Rudich, R. K. Talukdar, R. W. Fox, and A. R. Ravishankara, J. Phys. Chem. **100**, 5374 (1996).

2 E. S. C. Kwok, S. M. Aschmann, J. Arey, and R. Atkinson, Int. J. Chem. Kinet. **28**, 925 (1996).

3 A. A. Chew, R. Atkinson, and S. M. Aschmann, J. Chem. Soc. Faraday Trans. **94**, 1083 (1998).

4 C. E. Canosa-Mas, S. Carr, M. D. King, D. E. Shallcross, K. C. Thompson, and R. P. Wayne, Phys. Chem. Chem. Phys. **1**, 4195 (1999).

5 IUPAC (2002), http://www.iupac-kinetic.ch.cam.ac.uk/

6 R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).