IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC17

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

NO_3 + CH_2=CHC(O)CH_3 (methyl vinyl ketone) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
≤1.2 x 10^{-16}	298	Rudich et al., 1996	F-A (a)
Relative Rate Coefficients			
<6 x 10^{-16}	296 ± 2	Kwok et al., 1996	RR (b)
(5.0 ± 1.2) x 10^{-16}	296 ± 2	Canosa-Mas et al., 1999	RR (c)

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. A rate coefficient of (1.0 ± 0.2) x 10^{-16} cm^3 molecule^{-1} s^{-1} was measured but an upper limit cited because of the difficulty in measuring such low reaction rate coefficients.[1]

(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 methyl vinyl ketone and propene (the reference compound) were measured by GC. The measured upper limit to the rate coefficient ratio of k(NO_3 + methyl vinyl ketone)/k(NO_3 + propene) <0.06 is placed on an absolute basis by use of a rate coefficient of k(NO_3 + propene) = 9.29 x 10^{-15} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

(c) 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 methyl vinyl ketone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(NO_3 + methyl vinyl ketone)/k(NO_3 + ethene) = 2.53 ± 0.59 is placed on an absolute basis by use of a rate coefficient of k(NO_3 + ethene) = 1.96 x 10^{-16} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation). An absolute rate coefficient of (3.2 ± 0.6) x 10^{-16} cm^3 molecule^{-1} s^{-1} was also measured at 296 ± 1 K using a discharge flow system with LIF detection of NO_3 radicals.

Preferred Values

k <6 x 10^{-16} cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The rate coefficient measured in the relative rate study of Canosa-Mas et al. (1999) is consistent with the upper limit obtained by Kwok et al. (1996) but not with the rate coefficient

(or cited upper limit) determined in the absolute rate study of Rudich et al. (1996). Although Canosa-Mas et al. (1999) also obtained an absolute rate coefficient in reasonable agreement with their relative rate coefficient, the absolute rate coefficient must be viewed as an upper limit because of the potential for secondary reactions (as observed by Canosa-Mas et al. (1999) in the same study for the reactions of NO_3 radicals with acrolein and methacrolein).
The preferred upper limit to the rate coefficient is that measured by Kwok et al. (1996) and is sufficiently high to encompass the rate coefficients obtained by Canosa-Mas et al. (1999).

References

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Kwok, E. S. C., Aschmann, S. M., Arey, J. and Atkinson, R.: Int. J. Chem. Kinet., 28, 925, 1996.

Rudich, Y., Talukdar, R. K., Fox, R. W. and Ravishankara, A. R.: J. Phys. Chem., 100, 5374, 1996.