

IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet NO3_VOC16

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NO₃ + CH₃C(O)CH=CH₂ (methyl vinyl ketone) → products**Rate coefficient data**

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

Comments

- (a) NO₃ radicals were generated by thermal decomposition of N₂O₅ 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 cm³ 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. NO₃ radicals were generated by thermal decomposition of N₂O₅. 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*(NO₃ + methyl vinyl ketone)/*k*(NO₃ + propene) < 0.06 is placed on an absolute basis by use of a rate coefficient of *k*(NO₃ + propene) = 9.29 x 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ at 296 K.⁴
- (c) Relative rate method carried out at atmospheric pressure of N₂. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of methyl vinyl ketone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of *k*(NO₃ + methyl vinyl ketone)/*k*(NO₃ + ethene) = 2.53 ± 0.59 is placed on an absolute basis by use of a rate coefficient of *k*(NO₃ + ethene) = 1.96 x 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ at 296 K.⁴ An absolute rate coefficient of (3.2 ± 0.6) x 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ was also measured at 296 ± 1 K using a discharge flow system with LIF detection of NO₃ radicals.

Preferred Values

k < 6 x 10⁻¹⁶ cm³ 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.*³ is consistent with the upper limit obtained by Kwok *et al.*² but not with the rate coefficient (or cited upper limit) determined in the absolute rate study of Rudich *et al.*¹ Although Canosa-Mas *et al.*³ 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.*³ in the same study for the reactions of NO₃ radicals with acrolein and methacrolein).

The preferred upper limit to the rate coefficient is that measured by Kwok *et al.*² and is sufficiently high to encompass the rate coefficients obtained by Canosa-Mas *et al.*³

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 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).
- ⁴ IUPAC (2002), <http://www.iupac-kinetic.ch.cam.ac.uk/>