

IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet NO3_VOC13Website: <http://www.iupac-kinetic.ch.cam.ac.uk/>. See website for latest evaluated data.

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This datasheet updated: 25th November 2004.**NO₃ + (CH₃)₂CHCHO → products****Rate coefficient data**

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
2.9 x 10 ⁻¹² exp[-(1685 ± 120)/T] (0.9 ± 0.1) x 10 ⁻¹⁴	264-364 298	Ullestam, Langer and Ljungstrom, 2000	DF-LPA (a)
1.0 x 10 ⁻¹⁰ exp[-(2598 ± 384)/T] (1.61 ± 0.13) x 10 ⁻¹⁴	298-433 298	Cabanas et al., 2003	DF-LIF (b)
<i>Relative Rate Coefficients</i>			
(1.26 ± 0.14) x 10 ⁻¹⁴	298	D'Anna and Neilsen, 1997	RR-FTIR (c)
(1.20 ± 0.20) x 10 ⁻¹⁴	298	Ullestam, Langer and Ljungstrom, 2000	RR-FTIR (d)

Comments

- (a) NO₃ radicals were generated by F + HNO₃ reaction at 2.5 mbar total pressure and monitored by long path absorption at 661.8 nm; pseudo first order conditions. Experiments conducted with and without 20% O₂ added to the He carrier gas to inhibit suspected secondary reactions. With added O₂ the rate coefficients were approximately a factor of 3 lower, but showed a similar *E_a*. The cited 298 K value was obtained in the presence of O₂; the Arrhenius expression was obtained by correction of all data for contribution of secondary reactions.
- (b) NO₃ radicals were generated by F + HNO₃ reaction at 1.5 mbar total pressure, and monitored by LIF excited at 662 nm. Secondary reactions were considered to be unimportant but no supporting tests were reported.
- (c) Relative rate method carried out at 1013 mbar pressure of air. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of 2-methylpropanal and 1-butene (the reference compound) were measured by GC. The resulting rate coefficient ratio of *k*(NO₃ + 2-methylpropanal)/*k*(NO₃ + 1-butene) = 0.93 ± 0.10 is placed on an absolute basis by use of a rate coefficient of *k*(NO₃ + 1-butene) = 1.35 x 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ at 298 K (Atkinson, 1997).
- (d) Relative rate method carried out at 1013 mbar pressure of air. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of 2-methylpropane and propenal (the reference compound) were measured by GC. The resulting rate coefficient ratio of *k*(NO₃ + 2-methylpropanal)/*k*(NO₃ + propene) = 1.3 ± 0.10 is placed on an absolute basis by use of a rate coefficient of *k*(NO₃ + propene) = 9.5 ± 1.2 x 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ at 298 K (IUPAC, 2004).

Preferred Values

$k = 1.25 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.67 \times 10^{-12} \exp(-1460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260-420 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature rate coefficients from relative rate measurements are in excellent agreement. The results of the absolute determinations are in less good agreement and are higher; the measurements are complicated by secondary reactions leading to excessive NO₃ loss. Ullestram et al. (2000) show that the observed rate coefficient is reduced in the presence of O₂ due to suppression of the secondary reactions. Their value of k at 298 K with O₂ present is within experimental uncertainty of the relative rate values. The preferred value at 298 K is a mean of the values from the relative rate studies.

The temperature dependence of the rate coefficient was only investigated in the absolute studies. Ullestram et al. (2000) observed a similar activation energy both with and without O₂ present suggesting that the temperature dependence is not influenced significantly by secondary reactions. The data of Cabanas et al. above 298 K actually agree well with those of Ullestram et al. (2000) (without O₂); their apparently larger temperature dependence and unreasonably high A-factor, results from inclusion of the lower 298 K value, which must be considered suspect without proper correction for secondary reactions. The preferred temperature dependence adopts the E/R value of Ullestram et al. (2000) with an A factor adjusted to give the preferred value of k at 298 K.

The reaction products are likely to be HNO₃ + (CH₃)₂CHC(O).

References

- Atkinson, R.: J. Phys. Chem. Ref. Data 26, 215, 1997.
Cabanas, B., Salgado, S., Martin, M. T., Albaladejo, J. and Martinez, E.: Phys. Chem. Chem. Phys., 5, 112, 2003.
D'Anna, B., Andresen, O., Gefen, Z. and Nielsen, C. J.: Phys. Chem. Chem. Phys., 3, 3057, 2001.
Ullestram, M., Langer, S. and E. Ljungstrom,: Int. J. Chem. Kinet. 28, 925, 1996.
IUPAC, <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2004.

