

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC15

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NO₃ + (CH₃)₂CHCHO → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$2.9 \times 10^{-12} \exp[-(1685 \pm 120)/T]$	264-364	Ullestam, Langer and Ljungstrom, 2000	DF-LPA (a)
$(0.9 \pm 0.1) \times 10^{-14}$	298		
$1.0 \times 10^{-10} \exp[-(2598 \pm 384)/T]$	298-433	Cabanas et al., 2003	DF-LIF (b)
$(1.61 \pm 0.13) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$(1.26 \pm 0.14) \times 10^{-14}$	298	D'Anna and Neilsen, 1997	RR-FTIR (c)
$(1.20 \pm 0.20) \times 10^{-14}$	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 $k(\text{NO}_3 + 2\text{-methylpropanal})/k(\text{NO}_3 + 1\text{-butene}) = 0.93 \pm 0.10$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + 1\text{-butene}) = 1.35 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 $k(\text{NO}_3 + 2\text{-methylpropanal})/k(\text{NO}_3 + \text{propene}) = 1.3 \pm 0.10$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.5 \pm 1.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 NO_3 loss. Ullestram et al. (2000) show that the observed rate coefficient is reduced in the presence of O_2 due to suppression the secondary reactions. Their value of k at 298 K with O_2 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 O_2 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 O_2); 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 $\text{HNO}_3 + (\text{CH}_3)_2\text{CHC}(\text{O})$.

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.

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